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LI.—ON MUCOXYBROMIC AND MUCOXYCHLORIC ACIDS.[1]

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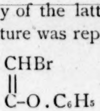
The action of baric hydrate upon mucobromic acid was studied several years ago by O. R. Jackson and one of us.[2] It was found that mucobromic acid was decomposed by a large excess of baric hydrate with the formation of α,β dibromacrylic and formic acids, while an essentially different reaction ensued in a feebly alkaline solution. The main product in this case was shown to be a dibasic acid containing four atoms of carbon; but it was not further studied. Somewhat later, E. K. Stevens and one of us[3] found that mucophenoxybromic acid was formed by an analogous reaction when mucobromic acid was treated with potassic phenylate; and the constitution of this acid was established with little difficulty by its conversion into phenoxybrommaleic and phenoxybromacrylic acids. The great stability of the latter acid in alkaline solution left no doubt that its structure was represented by the formula



$$\begin{array}{l} \mathrm{CHBr} \\ \| \\ \mathrm{C\text{-}O.C_6H_5} \\ | \\ \mathrm{COOH.} \end{array}$$

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[1] From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors.

[2] Proceedings American Academy **16**, 188.

[3] This Journal **6**, 187; and Proceedings **19**, 262.

While it was thus rendered probable that in the corresponding decompositions by baric hydrate an atom of bromine in the mucobromic acid had been replaced by hydroxyl, and the empirical formula of the product formed also warranted this conclusion, it was difficult to obtain any definite experimental evidence in its support. The isomerism of this acid with monobrommaleic and monobromfumaric acid, and its strongly marked dibasic character, made its constitution a question of decided interest. We therefore undertook its more extended investigation, as well as a study of the analogous chlorine compound, which could readily be obtained from mucochloric acid. Although our investigations are in many respects incomplete, they seem to us to leave little doubt as to the constitution of the compounds in question; and since we shall be unable to continue the work together, we have thought it best to present the results which we have already obtained.

Mucoxybromic Acid.

Whenever mucobromic acid is dissolved in a solution of an alkaline hydrate, more or less mucoxybromic acid appears to be formed. For its preparation, however, we have found it necessary to use baric hydrate, and the yield is then largely dependent upon the conditions under which the reaction takes place. We have found it most advantageous to suspend the mucobromic acid in thirty parts of cold water, and, after cooling well with ice, to add gradually, with constant shaking, finely powdered baric hydrate of known strength. After the mucobromic acid is neutralised, the baric hydrate must be added in small quantities, and the solution allowed to stand until the alkaline reaction has nearly disappeared before a fresh portion is added. The alkaline reaction disappears rapidly at first, afterwards more slowly, and when the amount of baric hydrate demanded by the equation

$$2C_4H_2Br_2O_3 + 3BaO_2H_2 = 2BaC_4HBrO_4 + BaBr_2 + 4H_2O$$

has been added, the reaction usually remains feebly alkaline, even after long standing. The slight excess of baric hydrate is then removed by carbonic dioxide, and an equal volume of alcohol added to the filtered solution. Baric mucoxybromate, which is very sparingly soluble in dilute alcohol, is thus precipitated in the form of fine, flattened, pointed needles, and may be purified by dissolving in cold water and reprecipitating with alcohol. With careful work, about sixty per cent. of the theoretical yield may be obtained. The preparation of the free acid from the barium salt is a matter of considerable difficulty, since it cannot be extracted from aqueous solution by the ordinary solvents, and it is quickly decomposed during the evaporation of its solution, even at ordinary temperatures. We succeeded in preparing it only by moistening the salt with a little water, precipitating the barium exactly with sulphuric acid, and evaporating the concentrated solution of the acid thus obtained as rapidly as possible over sulphuric acid in vacuo. The viscous residue thus obtained gradually solidified at low temperatures, and yielded tolerably well-formed thick prisms with beveled ends. The substance, freed from the viscous mother liquors as completely as possible and dried over sulphuric acid, gave, on analysis, the following results:

I. 0.7181 gram substance gave 0.6451 gram CO_2 and 0.1004 gram H_2O.

II. 0.7504 gram substance gave 0.6697 gram CO_2 and 0.1010 gram H_2O.

III. 0.2053 gram substance gave 0.1977 gram AgBr.

IV. 0.2348 gram substance gave 0.2254 gram AgBr.

	Calculated for $C_4H_3BrO_4$.	Found.			
		I.	II.	III.	IV.
C	24.60	24.50	24.34		
H	1.54	1.55	1.50		
Br	41.03	...	...	41.00	40.86

Mucoxybromic acid is extremely soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. The melting point was found to be 111°–112°; the true melting point may, however, be somewhat higher, since the substance could not be purified by repeated crystallisation. The acid gives with ferric chloride an intense garnet-red coloration, which is readily seen, even in very dilute solutions. With argentic nitrate it gives a white crystalline precipitate of the silver salt. Baric acetate added to a concentrated aqueous solution throws down the highly crystalline barium salt. By the action of hydrobromic acid saturated at 0°, or of phosphoric pentabromide, no definite products were obtained.

Baric Mucoxybromate, $BaC_4HBrO_4.2H_2O$.—The preparation of the barium salt has already been described. The salt is somewhat sparingly soluble in cold water, and its solubility is not sensibly increased by heat. It is rapidly decomposed by boiling its aqueous solution, and even in the cold decomposition ensues after long standing. On the evaporation of a solution saturated at ordinary temperatures over sulphuric acid in vacuo, the salt separates in long lustrous six-sided prisms with perpendicular terminations. The air-dried salt loses over sulphuric acid, or at 100°, rather more than one molecule of water, and has then the composition $BaC_4HBrO_4.H_2O$. When heated to 105°-115°, it slowly loses the second molecule of water, but at the same time it turns brown, and baric bromide is formed.

I. 1.5527 grams of the salt, crystallised from water and dried by exposure to the air, lost over sulphuric acid 0.0953 gram H_2O.

II. 1.0746 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0663 gram H_2O.

III. 1.0502 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0631 gram H_2O.

	Calculated for $BaC_4HBrO_4.2H_2O$.	Found. I.	II.	III.
$1H_2O$	4.92	6.14	6.17	6.01

The salt dried over sulphuric acid gave, on analysis, the following results:

I. 0.2769 gram of the salt gave 0.1837 gram $BaSO_4$.

II. 0.2052 gram of the salt gave 0.1368 gram $BaSO_4$.

III. 0.5470 gram of the salt gave 0.3678 gram $BaSO_4$.

IV. 0.4128 gram of the salt gave 0.2079 gram CO_2 and 0.0354 gram H_2O.

V. 0.4988 gram of the salt gave 0.2516 gram CO_2 and 0.0477 gram H_2O.

VI. 0.2120 gram of the salt gave 0.1128 gram AgBr.

VII. 0.2684 gram of the salt gave 0.1457 gram AgBr.

	Calculated for $BaC_4HBrO_4.H_2O$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
Ba	39.37	39.00	39.19	39.54				
C	13.77	...	...	...	13.74	13.76		
H	0.86	...	...	...	0.95	1.06		
Br	22.99	...	...	...	...	...	22.64	23.11

We have made many unsuccessful attempts to prepare an acid barium salt. In every case, when the acid solution was precipitated with alcohol, or evaporated in vacuo over sulphuric acid, we obtained only the neutral salt.

Potassic Mucoxybromate, $K_2C_4HBrO_4.H_2O$.—The potassium salt was prepared from the barium salt by exact precipitation with potassic carbonate, and evaporation of the solution thus obtained in vacuo. It crystallised in well-formed rhombic plates, which were very soluble even in cold water. On warming the solution, decomposition quickly ensued. The air-dried salt lost nothing over sulphuric acid, turned somewhat brown at 70°, but did not lose sensibly in weight until heated to 100°.

I. 0.4951 gram of the air-dried salt lost, at 100°, 0.0344 gram H_2O, and gave 0.2991 gram K_2SO_4.

II. 0.4604 gram of the air-dried salt lost, at 100°, 0.0307 gram H_2O, and gave 0.2780 gram K_2SO_4.

III. 0.5428 gram of the air-dried salt gave 0.3281 gram K_2SO_4.

	Calculated for $K_2C_4HBrO_4.H_2O$.	Found. I.	II.	III.
K	27.04	27.12	27.10	27.14
H_2O	6.64	6.95	6.67	

Argentic Mucoxybromate, $Ag_2C_4HBrO_4$. — Argentic nitrate added to a solution of the free acid, or one of its salts, throws down a crystalline precipitate of the silver salt. When this is warmed with water, argentic bromide is at first formed, then reduction takes place. When heated in a slightly ammoniacal solution, it is immediately blackened. It dissolves readily in dilute nitric acid, but the solution soon grows turbid with the separation of argentic bromide. The dry salt explodes on heating, or on moistening with concentrated nitric acid. For analysis, the salt was made by precipitating an excess of argentic nitrate with a dilute solution of the barium salt.

I. 0.3974 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.3634 gram AgBr.

II. 0.5478 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.5034 gram AgBr.

III. 0.5455 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr, 0.4999 gram AgBr.

IV. 0.5866 gram of the salt dried in vacuo over H_2SO_4 gave, on heating in sealed tube with diluted nitric acid, 0.2672 gram AgBr.

	Calculated for $Ag_2C_4HBrO_4$.	Found. I.	II.	III.	IV.
Ag	52.82	52.53	52.78	52.64	
Br	19.56	...	...	...	19.38

A solution of the barium salt yielded, with plumbic nitrate, a heavy yellow semi-crystalline precipitate, which, when dried over sulphuric acid, gave on analysis percentages of lead and bromine which only approximated those required by the formula PbC_4HBrO_4.

Dimethyl Mucoxybromate, $C_4HBrO_4(CH_3)_2$.—The dimethyl ether of mucoxybromic acid can readily be formed by the action of methyl iodide upon the dry silver salt. If the methyl iodide is slowly added to the silver salt, so much heat is evolved that a violent and even dangerous explosion ensues. The silver salt must therefore be added in small portions to an excess of methyl iodide, or must be suspended in dry ether before adding the methyl iodide. The product of the reaction proved to be a viscous, sticky liquid, which showed no signs of crystallisation after long standing over sulphuric acid in vacuo, and which could not be volatilised, even in vacuo, without decompositition. The substance dried over sulphuric acid in vacuo for several days gave somewhat too low a percentage of bromine.

0.3653 gram substance gave 0.3031 gram AgBr.

	Calculated for $C_4HBrO_4(CH_3)_2$.	Found.
Br	35.88	35.30

Diethyl Mucoxybromate, $C_4HBrO_4(C_2H_5)_2$.—This substance we attempted to prepare by the action of ethyl iodide diluted with dry ether upon the silver salt. We obtained a thick viscous product, which we were unable to purify, and which, after long standing over sulphuric acid in vacuo, proved to contain iodine, and gave too high a percentage of halogen.

I. 0.2288 gram substance gave 0.1911 gram AgBr.
II. 0.2328 gram substance gave 0.1920 gram AgBr.

	Calculated for $C_4HBrO_4(C_2H_5)_2$.	Found.	
		I.	II.
Br	31.82	35.56	35.10

The ether was decomposed by an excess of baric hydrate, the excess of baric hyrate precipitated by carbonic dioxide, and alcohol added to the filtrate solution. We obtained in this way a crystalline salt, which possessed all the properties of baric mucoxybromate.

0.5875 gram of the air-dried salt gave 0.3720 gram $BaSO_4$.

	Calculated for $BaC_4HBrO_4.2H_2O$.	Found.
Ba	37.43	37.23

Monoethyl Mucoxybromate, $C_4H_2BrO_4.C_2H_5$.—If ordinary ether is used instead of anhydrous ether in the preparation of the ethyl ether, the acid ether is obtained. We added the dry silver salt slowly to an excess of ethyl iodide, and after the first reaction was over, warmed for a short time on the water-bath. The product was then extracted with ordinary ether, and the ethereal extract allowed to evaporate spontaneously. The syrupy residue thus obtained gradually yielded an abundance of clear prisms with oblique truncations, which were pressed out and recrystallised from boiling benzol.

0.2068 gram of substance dried over H_2SO_4 gave 0.1762 gram AgBr.

	Calculated for $C_4H_2BrO_4.C_2H_5$.	Found.
Br	35.88	36.25

The monoethyl mucoxybromate dissolves quite readily in water, its solution has a strongly acid reaction, and gives with ferric chloride an intense red coloration. It dissolves readily in alcohol, ether, chloroform, or hot benzol, more sparingly in ligroin or carbonic disulphide. The melting point of the substance repeatedly recrystallised from benzol was found to be 88°–89°.

Decomposition in Alkaline Solution.

The instability of mucoxybromic acid and its salts in aqueous solution led us to study the reaction more closely, with the hope that the products of this decomposition might throw light upon the constitution of the acid. When a solution of the barium salt is heated to boiling, it soon acquires an acid reaction, and before long grows turbid, with the separation of acid baric oxalate. The reaction then appears to progress slowly, and even after long boiling the decomposition is incomplete. In an alkaline solution, however, complete decomposition is readily effected. Baric hydrate appears to have no action upon mucoxybromic acid in the cold. After standing for days the solution is still clear, and contains no baric bromide. On heating, baric oxalate and baric carbonate are soon thrown down, and in solution may then be found baric bromide and baric formiate. The barium salts which were precipitated on boiling were collected on a filter, and the presence of oxalic and carbonic acids proved by qualitative tests. The oxalic acid was then converted into the calcium salt, and its identity further established by analysis.

0.3141 gram of the salt dried at 100° gave 0.2883 gram $CaSO_4$.

Calculated for $CaC_2O_4.H_2O$.	Found.
27.39	27.01

The alkaline solution filtered from the precipitated baric oxalate and carbonate was freed from the excess of baric hydrate by carbonic dioxide, and concentrated by evaporation on the water-bath. It gave with argentic nitrate a heavy precipitate of argentic bromide, and the filtered solution, containing an exces of argentic nitrate, deposited metallic silver on heating. After removing the barium with dilute sulphuric acid, the solution yielded an acid distillate, from which plumbic formiate was obtained by neutralising with plumbic carbonate.

0.2498 gram of the salt dried over H_2SO_4 gave 0.2542 gram $PbSO_4$.

Calculated for $Pb.(CHO_2)_2$.	Found.
69.69	69.50

Beside baric formiate and baric bromide the aqueous solution contained, in small but not insignificant quantity, an amorphous gummy barium salt, whose nature we have been unable to determine, since all our attempts to convert it into a compound fit for analysis have proved unsuccessful. The formation of this gummy barium salt, together with the fact that quantitative determinations of the amounts of carbonic and oxalic acid formed in the reaction showed no simple ratio between the two, leaves little doubt that the reaction is essentially complex in its nature. When an aqueous solution of baric mucoxybromate is boiled with the addition of baric carbonate, the products of the decomposition appear to be the same. The action of water upon the free acid, which is doubtless similar, we have not yet studied in detail.

Action of Bromine in Aqueous Solution.

By the action of most of the ordinary oxidising agents upon mucoxybromic acid or its salts, we were unable to obtain any definite oxidation products except oxalic acid. Bromine water, however, gave us more satisfactory results. On adding bromine slowly to an aqueous solution of the acid, the color of the bromine rapidly disappeared, oxalic acid was formed, and at the same time a well-defined product containing bromine could be isolated. We found that the same reaction ensued, and apparently rather more neatly, when the barium salt was taken instead of the free acid. Two molecules of bromine were therefore added to a dilute solution of the barium salt. After standing for several hours, the color of the bromine had completely disappeared, and crystals of acid baric oxalate had separated in abundance. The strongly acid solution was then neutralised with calcic carbonate, filtered, and extracted with ether. The ether left, on evaporation, a syrupy residue, which gradually deposited well-formed oblique prisms, which melted at 51°–52°. The melting point of the substance, its characteristic crystalline form, and its reactions with alkalies and argentic nitrate, left little doubt that it was bromal hydrate, although the percentage of bromine which it gave on analysis was somewhat too low.

0.1351 gram substance gave 0.2534 gram AgBr.

	Calculated for $C_2Br_3H_3O_2$.	Found.
Br	80.26	79.84

We found that the purification of this substance by recrystallisation was attended with so great loss that we could hardly draw any definite conclusion as to the composition of the main product from analyses of the small purified residue, and we therefore determined to examine the products formed from it by the action of alkalies. Instead of extracting with ether the solution neutralised with calcic carbonate, we added to it a slight excess of potassic hydrate, and distilled, after neutralising the slightly alkaline solution with hydrochloric acid. In this way we obtained a colorless, heavy oil, which was easily recognised as bromoform. After drying over fused calcic chloride, it boiled at 147°–150°, under a pressure of 748 mm. Its identity was further established by analysis.

I. 0.1739 gram substance gave 0.3893 gram AgBr.
II. 0.2202 gram substance gave 0.4940 gram AgBr.

	Calculated for $CHBr_3$.	Found.	
		I.	II.
Br	94.86	95.28	95.48

The weight of bromoform thus obtained amounted to between sixty and seventy per cent. of that required by the assumption that each molecule of the acid yielded one molecule of bromal.

The residue left after distilling off the bromoform was then acidified and distilled with steam. The acid distillate contained formic acid, as was shown by the ordinary qualitative tests and by the analysis of the lead salt prepared from it.

0.3193 gram of the salt dried at 100° gave 0.3256 gram $PbSO_4$.

	Calculated for $Pb.(CHO_2)_2$.	Found.
Pb	69.69	69.66

One of the products of the reaction was therefore bromal. In the insoluble residue removed by filtration after neutralising with calcic carbonate was found oxalic acid in abundance, which was identified by qualitative reactions and by the analysis of its calcium salt.

0.3779 gram of the salt dried at 100° gave 0.3490 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.39	27.16

The decomposition of mucoxybromic acid by aqueous bromine may therefore be expressed by the equation

$$C_4H_3BrO_4 + 2Br_2 + H_2O = C_2HBr_3O + H_2C_2O_4 + 2HBr.$$

Although phenylhydrazine readily reacts upon mucoxybromic acid, even in dilute solution, the flocculent product formed rapidly turns brown, and we have not succeeded in obtaining it in a form fit for analysis. Hydroxylamine also yielded no more satisfactory results, although we tried the reaction under a variety of conditions. On the other hand, the primary aromatic amines in neutral or acid solutions gave beautifully crystalline products with the greatest readiness. Aniline, parabromaniline, para- and metanitraniline, ortho- and paratoluidine, all yielded similar products, but we have thus far studied in detail the aniline compound alone. Urea likewise gives a crystalline condensation product which has not yet been further investigated.

Anilmucoxybromic Acid.

When aniline chloride is added to a dilute solution of mucoxybromic acid, the solution soon becomes yellow, and after a short time solidifies, with the separation of finely felted, light yellow needles. A moderate excess of free hydrochloric acid in no way interferes with the formation of the product, so that it may be most conveniently prepared by dissolving baric mucoxybromate in a slight excess of dilute hydrochloric acid, and adding a molecule of aniline dissolved in hydrochloric acid. The product was recrystallised from hot water, dried over sulphuric acid, and proved then to be anilmucoxybromic acid, formed according to the equation

$$C_4H_3BrO_4 + C_6H_5NH_2 = C_4H_3BrO_3.C_6H_5N + H_2O.$$

I. 0.2775 gram substance gave 0.4540 gram CO_2 and 0.0790 gram H_2O.

II. 0.2602 gram substance gave 0.1810 gram AgBr.

III. 0.2526 gram substance gave 0.1764 gram AgBr.

IV. 0.5563 gram substance gave 25.2 cc. of moist nitrogen at 19° and under a pressure of 748 mm.

	Calculated for $C_{10}H_8BrNO_3$.	Found. I.	II.	III.	IV.
C	44.44	44.62			
H	2.96	3.16			
Br	29.63	...	29.61	29.73	
N	5.18	...	...	...	5.21

The air-dried acid apparently contained one molecule of water, which it lost rapidly over sulphuric acid or when heated to 70°. At 100° a slow decomposition appeared to take place. The loss of crystal water was accompanied by a change of color to brilliant yellow.

I. 0.5579 gram of air-dried substance lost, at 62°-65°, 0.0362 gram H_2O.

II. 0.9504 gram of air-dried substance lost, at 70°, 0.0630 gram H_2O.

III. 1.0217 gram of air-dried substance lost over sulphuric acid 0.0786 gram H_2O.

	Calculated for $C_{10}H_8BrNO_3.H_2O$.	Found. I.	II.	III.
H_2O	6.25	6.49	6.63	7.69

Anilmucoxybromic acid crystallises from water in fine pale yellow needles, which are sparingly soluble in cold water, more readily in hot. On long heating of the aqueous solution decomposition sets in. The acid dissolves readily in alcohol, ether, or in hot chloroform or benzol; in ligroin or carbonic disulphide it is sparingly soluble. From chloroform it crystallises in small compact oblique prisms, which melt, with decomposition, at 131°-132°. The acid dissolves readily in solutions of the alkaline carbonates, and is reprecipitated unchanged on the addition of acids. With the salts of the heavy metals it gives brilliant yellow insoluble salts, and with ferric chloride it yields a deep brown precipitate. On heating with acids or alkalies, aniline is formed. On titration with baric hydrate two molecules of the acid were found to be neutralised by one molecule of baric hydrate, but salts containing two atoms of silver and potassium could also be prepared.

Monobaric Anilmucoxybromate, $Ba(C_{10}H_7BrNO_3)_2\frac{1}{2}H_2O$.—By the action of baric carbonate upon the acid suspended in water, a salt is formed which is somewhat sparingly soluble in hot or cold water. On evaporation of the solution a portion of the salt separates in yellow needles, but decomposition soon ensues. On the addition of baric acetate to the acid neutralised with ammonic hydrate, an amorphous flocculent precipitate was thrown down, which dissolved on heating, and immediately in its place there appeared a highly crystalline bright yellow precipitate. As the solution cooled, still more of the salt separated in felted needles. The air-dried salt apparently contained a half-molecule of crystal water, which it lost at 100°.

0.5802 gram of the air-dried salt lost, at 100°, 0.0075 gram H_2O.

	Calculated for $Ba.(C_{10}H_7BrNO_3)_2\frac{1}{2}H_2O$.	Found.
H_2O	1.32	1.25

0.5755 gram of this salt dried at 100° gave 0.1970 gram $BaSO_4$.

	Calculated for $Ba.(C_{10}H_7BrNO_3)_2$.	Found.
Ba	20.30	20.12

Diargentic Anilmucoxybromate, $Ag_2C_{10}H_6BrNO_3$. — When argentic nitrate was added to an aqueous solution of the free acid, a pale yellow gelatinous precipitate was thrown down, which apparently contained one atom of silver. If, however, the acid was dissolved in two equivalents of ammonic hydrate, and the solution was then added to an excess of argentic nitrate, a voluminous bright orange-yellow precipitate was thrown down, which on standing became dense and semi-crystalline, and contained two atoms of silver. When warmed with an excess of argentic nitrate in a feebly ammoniacal solution, no immediate reduction took place.

0.4275 gram of the salt dried over H_2SO_4 gave 0.3290 gram AgBr.

	Calculated for $Ag_2C_{10}H_6BrNO_3$.	Found.
Ag	44.64	44.21

Dipotassic Anilmucoxybromate, $K_2C_{10}H_6BrNO_3$.—On the addition of an alcoholic solution of potassic hydrate to a solution of the acid in anhydrous ether, a pale yellow salt was thrown down, which was well washed with anhydrous ether, and dried in vacuo over sulphuric acid and solid sodic hydrate.

0.3556 gram of the salt gave 0.1805 gram K_2SO_4.

Calculated for $K_2C_{10}H_6BrNO_3$.	Found.
22.58	22.79

While anilmucoxybromic acid forms by preference monobasic salts, it is evidently capable of exchanging two of its hydrogen atoms for metals.

Phenylhydrazine Anilmucoxybromate, $C_{10}H_8BrNO_3.C_6H_8N_2.H_2O$.—When phenylhydrazine hydrochlorate is added to anilmucoxybromic acid dissolved in a dilute solution of sodic acetate, a colorless crystalline precipitate soon separates, which, after washing with cold water, becomes somewhat discolored on drying. The compound is but sparingly soluble in cold water, more readily in hot, but it cannot be recrystallised from hot water without decomposition. It is readily soluble in alcohol, but nearly insoluble in ether. It is readily decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior showed the substance to be a simple salt of phenylhydrazine, and analysis also failed to show the elimination of water.

0.3708 gram of the air-dried substance gave 36.5 cc. of moist nitrogen at 25° under a pressure of 726 mm.

	Calculated for $C_{16}H_{16}BrN_3O_3.H_2O$.	Found.
N	10.60	10.77

Mucoxychloric Acid.

W. Z. Bennett[1] and one of us several years ago studied the action of baric hydrate upon mucochloric acid. It was found that the acid was decomposed by a large excess of baric hydrate, and that $\alpha\beta$ dichloracrylic and formic acids were formed in nearly theoretical quantities. When the baric hydrate is carefully added, so that the solution is at no time very strongly alkaline, the reaction follows an entirely different course, and mucoxychloric acid is found in abundance. Since the $\alpha\beta$ dichloracrylic acid had already been shown to be more stable than the corresponding dibromacrylic acid, we were led to study mucoxychloric acid more in detail, with the hope that its derivatives would also prove more stable and more manageable than those of mucoxybromic acid. In the preparation of mucoxychloric acid we followed precisely the same method which we had found advantageous with the bromine compound. Mucochloric acid[1] was suspended in 35 times its weight of water, and, after cooling well with ice, the theoretical quantity of finely powdered baric hydrate was slowly added, taking care to avoid at any time a large excess. After the requisite amount of baric hydrate had been added, we allowed the solution to stand over night, and removed the slight excess of baric hydrate, which was then usually found present, by means of carbonic dioxide. The filtered solution gave, when mixed with an equal volume of alcohol, a voluminous highly crystalline precipitate of baric mucoxychlorate, which could be purified by reprecipitation from aqueous solution by alcohol. In this way we have obtained 73 per cent. of the theoretical amount of barium salt demanded by the equation

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[1] Proceedings American Academy **16**, 206.

$$2C_4H_2Cl_2O_3 + 3BaO_2H_2 = 2BaC_4HClO_4 + BaCl_2 + 4H_2O.$$

The mother liquors contain, beside baric chloride, baric $\alpha\beta$ dichloracrylate, which may be obtained without difficulty by the evaporation of the solution. Although ether extracts the acid from aqueous solution, it does not take it up very readily, and we have found it more advantageous to precipitate the barium salt exactly with dilute sulphuric acid, and evaporate the aqueous solution thus obtained in vacuo over sulphuric acid. The acid may readily be recrystallised with care from a little warm water. For analysis the acid was dried over sulphuric acid.

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[1] Although W. Z. Bennett and I had succeeded in obtaining a fairly satisfactory yield of mucochloric acid, the method which we used was troublesome and tedious in the extreme when large quantities of material were involved, and necessitated the prolonged treatment of large quantities of liquid at 0° with chlorine gas. The slightest want of care also frequently diminished the yield most seriously. I therefore made many fruitless attempts to find some more advantageous method for its preparation. I at last hit upon an extremely convenient and simple method, which allows the preparation of any quantity of mucochloric acid desired in the course of a few hours. The yield is also quite satisfactory, and falls not far short of that which is attainable by the old method. Pyromucic acid is suspended in 14½ times its weight of common strong hydrochloric acid (sp. gr. 1.16), and somewhat more than four molecules of finely powdered manganic dioxide are then gradually added. At first the mixture is kept cold (ice cooling is unnecessary). The temperature is then allowed to rise, and finally the solution is heated and boiled gently for twenty minutes. Since it is difficult to filter the hot strongly acid liquid from the impurities contained in the manganic dioxide, the solution is allowed to cool, and the mucochloric acid which separates collected upon a filter of coarse cloth. It is then dissolved in hot water, and the filtered solution concentrated by evaporation if necessary. From 100 grams of pyromucic acid suspended in 1250 cc. of ordinary hydrochloric acid and 380 grams of manganese dioxide (83 per cent. MnO_2), 50 grams of pure mucochloric acid are readily obtained, and the mother liquors yield 2-3 grams of a somewhat dark-colored acid. Bennett and I obtained by the much more laborious method, as the result of many separate operations, 129 grams of mucochloric acid from 202 grams pyromucic acid. This method accordingly yields in a short time about 83 per cent. of the amount attainable by the more tedious method. —H. B. H.

I. 0.2925 gram substance gave 0.3420 gram CO_2 and 0.0615 gram H_2O.

II. 0.1990 gram substance gave 0.1915 gram AgCl.

III. 0.2000 gram substance gave 0.1918 gram AgCl.

	Calculated for $C_4H_3ClO_4$.	Found. I.	II.	III.
C	31.89	31.88		
H	1.99	2.33		
Cl	23.59	...	23.79	23.71

Mucoxychloric acid is readily soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. From water it crystallises in stout prisms with beveled ends, which melt at 114°-115°. With ferric chloride it gives, even in extremely dilute solutions, a deep garnet-red coloration. With argentic nitrate it gives an immediate crystalline precipitate of the silver salt. Although more stable than mucoxybromic acid, it is soon decomposed by warming its aqueous solution.

Baric Mucoxychlorate, $BaC_4HClO_4.2H_2O$.—The preparation of the barium salt has already been described. It is sparingly soluble in cold water, more readily in hot, and is nearly insoluble in dilute alcohol. Although it is decomposed by heating its aqueous solution, the decomposition is not particularly rapid, and small quantities of the salt may be recrystallised from hot water with little difficulty. It crystallises then in fine clustered needles, and is obtained in the same form by precipitating its aqueous solution with alcohol. In evaporating a cold aqueous solution in vacuo over sulphuric acid, the salt may be obtained in long lustrous prisms with perpendicular terminations. The salt crystallised from water, or precipitated by alcohol, when air-dried, loses over sulphuric acid somewhat more than one molecule of water, and has then the composition $BaC_4HClO_4.H_2O$.

I. 2.5352 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1706 gram H_2O.

II. 2.2127 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1480 gram H_2O.

III. 1.9160 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1288 gram H_2O.

IV. 1.5273 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1054 gram H_2O.

	Calculated for $BaC_4HClO_4.2HO_2$.	Found. I.	II.	III.	IV.
$1H_2O$	5.60	6.73	6.69	6.73	6.90

The salt dried over sulphuric acid contained a percentage of barium agreeing closely with that required by the formula $BaC_4HClO_4.H_2O$. It lost weight slowly at 100°–105°, but only the compact salt crystallised from water could be brought to constant weight at this temperature without essential decomposition. The voluminous salt precipitated by alcohol after many weeks still lost in weight, contained baric chloride, and had become badly discolored.

I. 1.4644 grams of salt recrystallised from water and dried over sulphuric acid lost, at 100°–105°, 0.0820 gram H_2O.

II. 1.4771 grams of salt recrystallised from water and dried over sulphuric acid lost, at 100°–105°, 0.0827 gram H_2O.

III. 0.8947 gram of salt recrystallised from water and dried over sulphuric acid gave 0.6871 gram $BaSO_4$.

IV. 0.5865 gram of salt recrystallised from water and dried over sulphuric acid gave 0.4498 gram $BaSO_4$.

V. 0.3261 gram of salt precipitated by alcohol and dried over sulphuric acid gave 0.3266 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.H_2O$.	Found. I.	II.	III.	IV.	V.
H_2O	5.93	5.60	5.60			
Ba	45.14	...	...	45.16	45.08	45.06

Although the crystallised baric mucoxychlorate suffers no change when exposed to the air for a week or more, after months of exposure it loses in weight and the clear prismatic crystals become opaque. The salt is then more sparingly soluble in water, and crystallises in small oblique prisms. These same oblique crystals are also occasionally deposited together with the long rectangular prisms on evaporating in vacuo the aqueous solution of the salt originally obtained. An analysis showed that these oblique prisms contained a percentage of barium required by a salt crystallising with one molecule of water. Although the crystalline form appeared to be persistent, we were able to detect no differences in the chemical behavior of the salt, or of the acid prepared from it, which would warrant the assumption that any radical change in its structure had taken place.

For analysis, the oblique prisms were well washed with cold water and dried by exposure to the air. The air-dried salt lost nothing over sulphuric acid, and lost weight but slowly at 100°.

0.4076 gram of air-dried salt gave 0.3131 gram $BaSO_4$.

	Calculated for $BaC_4HClO_4.H_2O$.	Found.
Ba	45.14	45.15

Potassic Mucoxychlorate, $K_2C_4HClO_4$.—The potassium salt we prepared by decomposing the barium salt with potassic carbonate and evaporating the filtered solution in vacuo over sulphuric acid. The salt separated in small tabular crystals, which were recrystallised from warm water. The air-dried salt lost nothing when heated at 100°.

I. 0.4344 gram of the salt gave 0.3334 gram K_2SO_4.

II. 0.4631 gram of the salt gave 0.3547 gram K_2SO_4.

	Calculated for $K_2C_4HClO_4$.	Found. I.	 II.
K	34.49	34.45	34.39

Argentic Mucoxychlorate, $Ag_2C_4HClO_4$.—The silver salt was made by precipitating a solution of argentic nitrate with a solution of the potassium salt. On heating, argentic chloride was rapidly formed. On warming with a little ammonic hydrate, immediate reduction ensued. From a solution of the free acid, argentic nitrate threw down the neutral salt (III).

I. 0.5024 gram of the salt dried over H_2SO_4 gave 0.3948 gram AgCl.

II. 0.4125 gram of the salt dried over H_2SO_4 gave 0.3240 gram AgCl.

III. 0.3704 gram of the salt dried over H_2SO_4 gave 0.2891 gram AgCl.

	Calculated for $Ag_2C_4HClO_4$.	I.	Found. II.	 III.
Ag	59.27	59.17	59.13	58.76

Diethyl Mucoxychlorate, $C_4HClO_4(C_2H_5)_2$.—Finely powdered argentic mucoxychlorate, which had been well dried over sulphuric acid, was gradually thrown into an excess of ethyl iodide. The heat evolved by the reaction was so great that the boiling point of the ethyl iodide was soon reached, and the decomposition was afterward completed by heating for a short time on the water-bath. The product of the reaction was then extracted by dry chloroform, the chloroform distilled off under diminished pressure, and the viscous residue placed over sulphuric acid in vacuo. After long standing in vacuo the product showed no signs of crystallisation, but proved to contain a percentage of chlorine which agreed tolerably well with that required by the diethyl ether.

0.2314 gram substance gave 0.1553 gram AgCl.

	Calculated for $C_4HClO_4(C_2H_5)_2$.	Found.
Cl	17.19	16.59

Monoethyl Mucoxychlorate, $C_4H_2ClO_4.C_2H_5$.—When the viscous diethyl ether just described was allowed to stand exposed to the air, or when it was mixed with a small quantity of water, it rapidly acquired an acid reaction, and gradually deposited well-formed crystals of the monoethyl ether. The latter could also readily be prepared by extracting with ordinary aqueous ether the product formed by the action of ethyl iodide upon the silver salt, and allowing the ethereal solution to evaporate spontaneously. The crystals which separated were thoroughly pressed and recrystallised from boiling benzol.

I. 0.2337 gram substance gave 0.3445 gram CO_2 and 0.0870 gram H_2O.

II. 0.2659 gram substance gave 0.2147 gram AgCl.

III. 0.2572 gram substance gave 0.2080 gram AgCl.

	Calculated for $C_4H_2ClO_4.C_2H_5$.	Found. I.	II.	III.
C	40.33	40.20		
H	3.92	4.13		
Cl	19.89	...	19.95	20.00

Monoethyl mucoxychlorate crystallises in clustered, obliquely truncated prisms, which melt at 94°-95°, and sublime unchanged at higher temperature. It dissolves readily in water, alcohol, ether, or chloroform, quite readily in boiling benzol, more sparingly in cold, and but sparingly in ligroin. Its aqueous solution is strongly acid to litmus, dissolves carbonates with effervescence, and gives a deep red coloration with ferric chloride. When baric hydrate is slowly added to the aqueous solution, a yellow color is developed, and products formed which we have not yet more fully studied. If, however, the ether is dissolved in an excess of baric hydrate, it is saponified and baric mucoxychlorate formed. The alkaline solution was precipitated with carbonic dioxide, and alcohol added to the filtered solution. The crystalline salt which separated was dissolved in cold water, and the solution evaporated over sulphuric acid in vacuo.

0.7070 gram of air-dried salt lost over sulphuric acid 0.0482 gram H_2O.

	Calculated for $BaC_4HClO_4.2H_2O$.	Found.
$1H_2O$	5.60	6.82

0.6588 gram of the salt dried over H_2SO_4 lost, at 100°, 0.0385 gram H_2O.

	Calculated for $BaC_4HCl.H_2O$.	Found.
H_2O	5.93	5.85

0.6203 gram of the salt dried at 100° gave 0.3535 gram $BaSO_4$.

	Calculated for BaC_4HClO_4.	Found.
Ba	47.98	47.85

Decomposition in Alkaline Solution.

The instability of mucoxychloric acid and its salts when heated in aqueous solution has already been mentioned. We have, however, as yet studied more closely only the reaction which takes place when baric mucoxychlorate is heated with an excess of baric hydrate. The solution soon grows turbid on boiling, and throws down baric oxalate and baric carbonate, while the solution then contains baric chloride and formiate. The insoluble salts were collected upon a filter, and the presence of carbonic and oxalic acids established by qualitative tests. The presence of oxalic acid was still further confirmed by an analysis of the calcium salt.

0.1740 gram of the salt dried at 100° gave 0.1608 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.39	27.17

The aqueous solution filtered from the insoluble salts was freed from the excess of baric hydrate by means of carbonic dioxide. It gave then with argentic nitrate an abundant precipitate of argentic chloride, and blackened when heated with an excess of argentic nitrate. The barium was removed by dilute sulphuric acid, and the filtered solution distilled. The acid distillate when neutralised with plumbic carbonate yielded plumbic formiate in characteristic form.

0.3244 gram of the salt dried at 100° gave 0.3327 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	70.06

As was the case with the corresponding decomposition of mucoxybromic acid, quantitative determinations of the amounts of oxalic and carbonic acid formed in the reaction showed no simple relation between the two, and at the same time products were formed in small but significant amounts, whose nature we have as yet been unable to determine.

Action of Bromine in Aqueous Solution.

Bromine acts readily upon an aqueous solution of mucoxychloric acid, and forms products strictly analogous to those formed from mucoxybromic acid under the same conditions. Since the chlorobromal hydrate proved to be even less manageable than the bromal hydrate, we thought it best to determine its presence, as before, from its decomposition products. Since the reaction seemed to be quite as neat with the salts as with the free acid, we added to a diluted aqueous solution of the barium salt two molecules of bromine, and allowed the mixture to stand at ordinary temperatures until the color of the bromine had completely disappeared. We then neutralised the strongly acid solution with calcic carbonate in the cold, and filtered. The insoluble residue thus obtained contained oxalic acid in abundance, and we were unable to detect in it any other organic constituent. The oxalic acid was converted into its calcium salt and analysed.

0.3489 gram of the salt dried at 100° gave 0.3212 gram $CaSO_4$.

	Calculated for $CaC_2O_4.H_2O$.	Found.
Ca	27.39	27.08

To the clear aqueous solution we added a slight excess of potassic hydrate, neutralised after a short time with hydrochloric acid, and distilled the neutral solution with steam. We obtained in this way a colorless heavy oil, which, when dried with calcic chloride, boiled without decomposition at 119°-120° under a pressure of 748 mm.[1] Analysis showed it to be dibromchlormethan.

I. 0.1545 gram substance gave 0.3855 gram AgCl + AgBr.
II. 0.1418 gram substance gave 0.3536 gram AgCl + AgBr.

	Calculated for $CHClBr_2$.	Found. I.	Found. II.
Cl + Br	93.74	93.91	93.85

The weight of dibromchlormethan thus obtained was about sixty per cent. of the theoretical amount.

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[1] According to O. Jacobsen and R. Neumeister (Ber. d. deutsch. chem. Gesellsch. **15**, 601), chlorobromoform boils between 123° and 125°, with slight decomposition.

The residue left after distillation was acidified, and again distilled with steam. The acid distillate thus obtained was neutralised with plumbic carbonate, and yielded upon evaporation plumbic formiate.

0.3936 gram of the salt dried at 100° gave 0.4003 gram $PbSO_4$.

	Calculated for $Pb(CHO_2)_2$.	Found.
Pb	69.69	69.47

The decomposition of mucoxychloric acid by aqueous bromine may therefore be expressed by the equation

$$C_4H_3ClO_4 + 2Br_2 + H_2O = H_2C_2O_4 + CClBr_2CHO + 2HBr.$$

Anilmucoxychloric Acid.

Mucoxychloric acid, like mucoxybromic acid, readily gives with phenylhydrazine a condensation product. It has, however, little stability, and we have therefore not studied it more closely. With aniline, however, it gives even in dilute acid solutions a beautifully crystalline product. For its preparation we added one molecule of aniline hydrochlorate to a solution of the barium salt in a slight excess of dilute hydrochloric acid. The solution soon turned yellow, and after standing for a short time solidified with the separation of pale yellow finely felted needles. At low temperatures the crystals formed were often nearly colorless. When recrystallised from hot water and dried over sulphuric acid, the substance was shown by analysis to be anilmucoxychloric acid formed according to the equation

$$C_4H_3ClO_4 + C_6H_5NH_2 = C_4H_3ClO_3.NC_6H_5 + H_2O.$$

I. 0.2146 gram substance gave 0.4170 gram CO_2 and 0.0791 gram H_2O.

II. 0.1797 gram substance gave 0.1142 gram AgCl.

III. 0.1865 gram substance gave 0.1186 gram AgCl.

IV. 1.0389 gram substance gave 60.6 cc. moist nitrogen at 23° and under a pressure of 746 mm.

	Calculated for $C_{10}H_8ClNO_3$.	Found.			
		I.	II.	III.	IV.
C	53.21	52.99			
H	3.54	4.10			
Cl	15.74	...	15.71	15.72	
N	6.21	...	...	...	6.60

The air-dried acid apparently contains one molecule of water of crystallisation, which it loses readily over sulphuric acid or when heated to 100°. With the loss of water the pale yellow or almost colorless needles become brilliant yellow.

I. 0.7579 gram of air-dried acid lost, at 100°, 0.0597 gram H_2O.

II. 0.9022 gram of air-dried acid lost, at 100°, 0.0702 gram H_2O.

III. 0.5646 gram of air-dried acid lost over H_2SO_4 0.0460 gram H_2O.

	Calculated for $C_{10}H_8ClNO_3$.	Found. I.	II.	III.
H_2O	7.39	7.88	7.78	8.15

Anilmucoxychloric acid is sparingly soluble in cold water, more readily in hot, and appears to suffer slow decomposition when its aqueous solution is boiled. It dissolves readily in alcohol or ether, sparingly in cold benzol or chloroform, more freely on heating. In ligroin or carbonic disulphide it is nearly insoluble. From chloroform it crystallises in small compact oblique prisms, which melt with decomposition at 145°-147°. The acid dissolves readily in solutions of the alkaline carbonates, and is reprecipitated unchanged by the addition of acids. In heating with acids or alkalies aniline is formed. An aqueous solution of the free acids gives deep yellow precipitates with salts of most of the heavy metals. With ferric chloride it gives a deep brown precipitate. It forms by preference monobasic salts, but we have prepared also dibasic salts.

Baric Anilmucoxychlorate, $Ba(C_{10}H_7ClNO_2)_2\frac{1}{2}H_2O$.—If baric carbonate is added to anilmucoxychloric acid suspended in cold water, carbonic dioxide is disengaged, and a barium salt readily soluble in water is formed. If the concentrated filtered solution is then heated nearly to boiling, it soon deposits abundant bright yellow clustered needles, which increase somewhat in quantity as the solution cools. The air-dried salt lost slightly in weight at 100°. This loss corresponded to about one half-molecule of crystal water; it is possible, however, that it was hygroscopic moisture alone.

I. 0.2819 gram of the air-dried salt lost, at 100°, 0.0052 gram H_2O.

II. 0.9735 gram of the air-dried salt lost, at 100°, 0.0196 gram H_2O.

	Calculated for $Ba(C_{10}H_7ClNO_3)_2\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	1.51	1.85	2.01

I. 0.2767 gram of the salt dried at 100° gave 0.1102 gram $BaSO_4$.

II. 0.3918 gram of the salt dried at 100° gave 0.1561 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_7ClNO_3)_2$.	Found.	
		I.	II.
Ba	23.37	23.42	23.42

Diargentic Anilmucoxychlorate, $Ag_2C_{10}H_6ClNO_3$.—When argentic nitrate is added to a cold aqueous solution of anilmucoxychloric acid, a pale yellow gelatinous precipitate is formed, which is hard to wash and prepare for analysis, and doubtless contains one atom of silver. If, however, the acid is dissolved in two equivalents of dilute ammonic hydrate, and this solution poured into an excess of argentic nitrate, a bright orange-yellow flocculent precipitate is thrown down, which becomes more compact on standing, and contains two atoms of silver. This salt showed but slight discoloration when warmed for some time with an excess of argentic nitrate in a feebly ammoniacal solution.

0.5431 gram of the salt dried over H_2SO_4 gave 0.3516 gram AgCl.

	Calculated for $Ag_2C_{10}H_6ClNO_3$.	Found.
Ag	49.15	48.73

Dipotassic Anilmucoxychlorate, $K_2C_{10}H_6ClNO_3$.—When an alcoholic solution of potassic hydrate was added, in slight excess, to a solution of anilmucoxychloric acid in dry ether, a pale yellow salt was precipitated, which when dried in vacuo over sulphuric acid and powdered sodic hydrate proved to contain two atoms of potassium.

0.6070 gram of the salt gave 0.3579 gram K_2SO_4.

	Calculated for $K_2C_{10}H_6ClNO_3$.	Found.
K	25.92	26.47

Phenylhydrazine Anilmucoxychlorate, $C_{10}H_8ClNO_3.C_6H_8N_2.H_2O$.—When phenylhydrazine hydrochlorate is added to anilmucoxychloric acid dissolved in a dilute solution of sodic acetate, a white crystalline substance soon separates, which becomes somewhat discolored on drying. It is sparingly soluble in cold water, readily soluble in alcohol, but insoluble in ether. It is decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior shows that it is simply a salt of phenylhydrazine rather than a characteristic condensation product. The substance was well washed with cold water and dried over sulphuric acid.

I. 0.3000 gram substance gave 0.1189 gram AgCl.

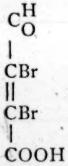
II. 0.3218 gram substance gave 34 cc. of moist nitrogen at 18° and under a pressure of 748 mm.

III. 0.2248 gram substance gave 23.5 cc. moist nitrogen at 20° and under a pressure of 741 mm.

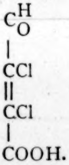
	Calculated for $C_{16}H_{16}ClN_3O_3.H_2O$.	Found. I.	II.	III.
Cl	9.98	9.80		
N	11.81	...	12.20	11.87

THEORETICAL CONSIDERATIONS.

Although the facts which we have observed are in certain respects difficult of interpretation, it seems to us that, on the whole, they warrant tolerably definite conclusions as to the constitution of mucoxybromic and mucoxychloric acids. We may safely assume that mucobromic and mucochloric acids are to be represented by the formulæ[1]



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CBr} \\ \| \\ \mathrm{CBr} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CCl} \\ \| \\ \mathrm{CCl} \\ | \\ \mathrm{COOH.} \end{array}$$

It is evident that the carboxyl group is not affected by the reaction in question, and, furthermore, that the aldehyde group is also still contained in the mucoxybromic and mucoxychloric acids. The latter fact is sufficiently proved by the behavior of the two acids with argentic nitrate, by the ready formation of condensation products with aniline, and, lastly, by the appearance of substituted aldehydes among the products formed from them by the action of aqueous bromine. The two central carbon atoms are therefore alone concerned in the transformation of mucobromic and mucochloric acids into the corresponding oxy-acids; and the first steps at least in this change must be the replacement of one of the halogen atoms by hydroxyl.

Since potassic phenylate acts upon mucobromic acid with the formation of mucophenoxybromic acid, whose constitution has been shown to be[2]

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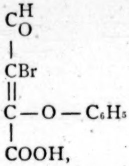
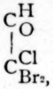
[1] Proceedings American Academy **16**, 218; **17**, 150.

[2] This Journal **6**, 194; and Proceedings American Academy **19**, 268.



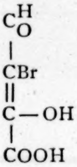
$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CBr} \\ \| \\ \mathrm{C-O-C_6H_5} \\ | \\ \mathrm{COOH,} \end{array}$$

it could safely be assumed that in the analogous reaction with baric hydrate the α-halogen atom would also be first replaced. The formation of dibromchlor aldehyde,

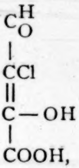


$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{C}^{\mathrm{Cl}}_{\mathrm{Br_2}}, \end{array}$$

by the action of bromine upon mucoxychloric acid, proves that this assumption is correct, since the β-chlorine atom has here retained its place. It follows, therefore, that the mucoxybromic and mucoxychloric acids are either hydroxyl acids formed by the replacement of the α-halogen atoms by hydroxyl,

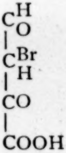


$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CBr} \\ \| \\ \mathrm{C-OH} \\ | \\ \mathrm{COOH} \end{array}$$

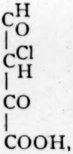


$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CCl} \\ \| \\ \mathrm{C-OH} \\ | \\ \mathrm{COOH,} \end{array}$$

or that they are the ketone acids,



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{C}^{\mathrm{Br}}_{\mathrm{H}} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{COOH} \end{array}$$

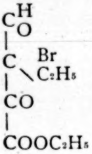


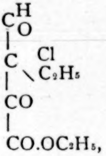
$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{C}^{\mathrm{Cl}}_{\mathrm{H}} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{COOH,} \end{array}$$

formed from them by the ordinarily observed molecular rearrangement.

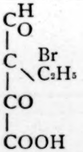
While a satisfactory explanation of the persistent dibasic character of the two acids can hardly be found in these formulæ, the formation of dibasic salts from either cannot be pronounced impossible, and no definite argument in favor of either formula can be based upon this behavior.

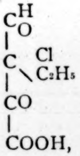
The ready and complete saponification of the ether of the two acids with the formation of the original dibasic metallic salts seems on the other hand an insurmountable objection to the ketone formula. The diethyl ethers of the ketone acids,





must of necessity yield upon saponification homologous monobasic acids,

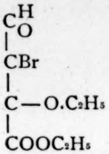




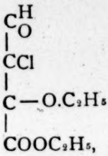
unless indeed a complete destruction of the molecule ensues.

We are therefore unable to resist the conclusion that mucoxybromic and mucoxychloric acids contain hydroxyl—that they are in fact phenol acids of the paraffine series, in which the hydroxyl has strongly marked acid properties on account of its peculiar environment.

The anomalous removal of the ethyl groups from the ethers,

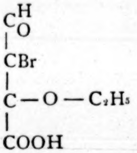


$$\begin{array}{l} CHO \\ | \\ CBr \\ | \\ C-O.C_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

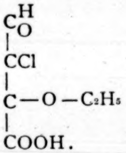


$$\begin{array}{l} CHO \\ | \\ CCl \\ | \\ C-O.C_2H_5 \\ | \\ COOC_2H_5, \end{array}$$

by saponification with baric hydrate, seems to us to be conditioned by the strongly acid character of this hydroxyl, a character which is usually wholly wanting. To the acid ethers formed by the action of water in the cold must be assigned the formulæ



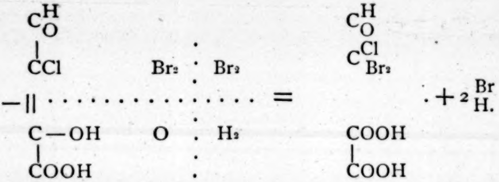
$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CBr} \\ | \\ \mathrm{C-O-C_2H_5} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} \\ | \\ \mathrm{CCl} \\ | \\ \mathrm{C-O-C_2H_5} \\ | \\ \mathrm{COOH}. \end{array}$$

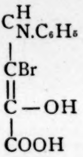
That these ethers are saponified by alkalies while the corresponding phenyl compounds are converted into derivatives of acrylic acid may possibly be due to the great difference in character between the phenyl and ethyl groups.

In other respects the behavior of the two acids finds ready explanation in the hydroxyl formulæ. While we are unable to follow in detail the somewhat complex reaction which ensues when the acids are heated with an excess of baric hydrate, the formation of oxalic, carbonic, and formic acids under these conditions is not unintelligible. The decomposition with aqueous bromine, on the other hand, evidently takes place according to the reaction

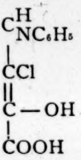


$$\begin{array}{lccccll} \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & & & & & \mathrm{C}^{\mathrm{H}}_{\mathrm{O}} & \\ | & & \vdots & & & & \\ \mathrm{CCl} & \mathrm{Br_2} & \vdots & \mathrm{Br_2} & & \mathrm{C}^{\mathrm{Cl}}_{\mathrm{Br_2}} & \\ -\| & \cdots\cdots\cdots & \cdots & \cdots\cdots & = & & \cdot + 2\,{}^{\mathrm{Br}}_{\mathrm{H}}. \\ \mathrm{C-OH} & \mathrm{O} & \vdots & \mathrm{H_2} & & \mathrm{COOH} & \\ | & & \vdots & & & | & \\ \mathrm{COOH} & & \cdot & & & \mathrm{COOH} & \end{array}$$

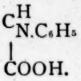
The aniline derivatives are then strictly analogous to the anilglyoxylic acid of Böttinger,[1]



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{N.C_6H_5}} \\ | \\ \mathrm{CBr} \\ \| \\ \mathrm{C-OH} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{NC_6H_5}} \\ | \\ \mathrm{CCl} \\ \| \\ \mathrm{C-OH} \\ | \\ \mathrm{COOH} \end{array}$$



$$\begin{array}{l} \mathrm{C}^{\mathrm{H}}_{\mathrm{N.C_6H_5}} \\ | \\ \mathrm{COOH}. \end{array}$$

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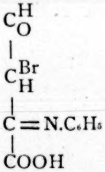
[1] Annalen der Chemie **198**, 222.

That the dibasic character of these compounds has been impaired by the introduction of the aniline residue is but natural, while the persistence of this dibasic character shows that they cannot be derived from the ketone formula by the replacement of the ketone oxygen. A compound of the form



$$\begin{array}{l} C^{H}_{O} \\ | \\ C^{Br}_{H} \\ | \\ C{=}N.C_6H_5 \\ | \\ COOH \end{array}$$

could hardly form dibasic salts.

Moreover, the fact that these aniline derivatives do not form stable condensation products with phenylhydrazine may be taken as further evidence that they contain hydroxyl, and not the ketone or aldehyde group. That we have not yet been able to reverse the reaction, and replace the hydroxyl groups again by the halogens, we cannot but think due simply to the instability of the acids themselves.

While we feel that the constitution of mucoxybromic and mucoxychloric acids is thus determined with reasonable certainty, further investigations upon the subject will be made in this laboratory.

ON THE DETERMINATION OF ARSENIC AS THE PENTASULPHIDE.

BY LEROY W. MCCAY.

In 1878 Bunsen,[1] in an article upon the separation of antimony from arsenic, showed that by treating an acidified solution of arsenic acid kept alternately hot and cold for a long time, with an excess of sulphuretted hydrogen, and permitting the whole to stand for a day, the arsenic was completely precipitated as the pentasulphide. He recommends this sulphide as an excellent form in which to determine arsenic.

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[1] Ann. d. Chem. **192**, 305.

I have of late been experimenting a good deal in connection with the conditions regulating the formation of the highest sulphide of arsenic, and have obtained the same results as those obtained by Bunsen. The precipitate obtained by passing a stream of sulphuretted hydrogen through the acidified solution of an alkali arseniate is undoubtedly pentasulphide of arsenic.[1]

Further, I have discovered a new and rapid method for preparing the sulphide by the action of sulphuretted hydrogen upon arsenic compounds, whereby it is obtained in a state of great purity. Aside from its theoretical importance, the method is of immediate value in its bearing upon the quantitative determination of arsenic. The principal objection to the Bunsen method lies in the long time and large quantities of sulphuretted hydrogen gas necessary to effect a complete separation. Chemists who have had any experience in the matter are well aware of how annoying the sluggish precipitation of arsenic by sulphuretted hydrogen from an arsenic acid solution can be. It will therefore doubtless prove a relief to many to know that a complete precipitation of the arsenic in the form of the pentasulphide is possible in one hour.

Some time ago I published in the *Chemical News*[2] an article upon the reduction of arsenic to arsenious acid by means of strong sulphurous acid, the reduction being accomplished in hermetically sealed bottles and at a temperature corresponding to that of a boiling water-bath. In a subsequent paper, which appeared in this Journal,[3] I showed how the idea could be made the basis of a method for estimating arsenic with great speed and accuracy.

Lately, while engaged in making some determinations of arsenic according to Bunsen's method, the thought struck me that perhaps the long and disagreeable precipitation of the arsenic might be avoided and the separation be easily and rapidly accomplished by making use of the same device employed in reducing arsenic to arsenious acid. A single experiment confirmed my expectations; the precipitation of the element was complete in one hour.[4] Indeed, the bottle had hardly been in the boiling bath a minute before the yellow pentasulphide commenced to come down. The bottle used in all my experiments has a capacity of about 200 cc. The stopper and neck of the bottle were treated with a little fine emery powder, so as to produce a perfectly air-tight joint. By wetting a small piece of cloth, stretching it down tightly over the stopper and tying the ends firmly to the sides of the neck of the bottle with a piece of cord also wetted, the danger of the stopper being thrown out during the heating is rendered very slight. I have generally thrown a piece of wire gauze over the bath during each experiment, but this is really unnecessary, as I have never yet had a bottle broken by the internal pressure.

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[1] This is in direct opposition to the statements of Ludwig, Wackenroder, H. Rose, and Fuchs.

[2] **51**, No. 1320, March 13, 1885.

[3] **7**, p. 373.

[4] See my preliminary note in the Chem. News **54**, 287.

A saturated solution of sulphuretted hydrogen, at the ordinary temperature, contains about three times its volume of the gas. 200 cc. of a dilute solution of arsenic acid would then absorb, roughly speaking, $200 \times 3 = 600$ cc. sulphuretted hydrogen gas. But 1000 cc. sulphuretted hydrogen gas $=$ 1.5199 grams; consequently 600 cc. gas $=$ 0.912 gram. Now, 150 grams As $=$ 160 grams S $=$ 170 grams H_2S for complete saturation. Hence the quantity of sulphuretted hydrogen absorbed by 600 cc. solution — namely, 0.912 gram — would suffice for precipitating 0.805 gram arsenic. But since the gas must be present in large excess,[1] the amount of arsenic capable of being precipitated as the pentasulphide would be considerably less than 0.805 gram. I have found anything from 0.1–0.3 gram to be a convenient quantity for a determination. The pentasulphide separates out in a thick skin, which adheres but slightly to the bottom and sides of the bottle. If the bottle, when cool, be inclined, the skin loosens itself, and one part can be made to overlap the other in a way which bears a striking resemblance to an omelette. The precipitate can be removed from the bottle without the slightest difficulty. When the sulphide, with the exception of a few particles, has been brought on the filter paper, a little water is put in the bottle, the stopper is inserted and the whole violently shaken for a few moments. Thus the particles are freed from any adhering air, are broken up, and can then be removed from the bottle so completely that not a yellow speck can be detected on the glass. I used for test analyses the following solutions:

1. $\frac{N}{10}$ solution of arsenic acid: This was prepared by oxidising 4.95 grams pure, dry arsenious acid with fuming nitric acid, evaporating, neutralising with ammonia and diluting to a litre.

2. A standard solution of di-hydrogen potassium arseniate: This was prepared by dissolving about 25 grams of the salt in

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[1] See Fresenius, Qualitative Analyse, 15te Auflage.

water and diluting to two litres. By careful analysis 25 cc. = 0.1292 gram As, and 50 cc. = 0.2585 gram As.

The first quantitative experiments were made precisely as follows:

A. The solution of arsenic acid was pipetted into the bottle, diluted to about 150 cc., and rendered strongly acid with concentrated hydrochloric acid. The solution was treated with sulphuretted hydrogen gas until a decided opalescence made its appearance, when the bottle was closed, the stopper firmly tied down, and the whole placed in the boiling water-bath and here kept for one hour. At the end of the hour the bottle was removed from the bath, allowed to cool, and violently shaken so as to cause the pentasulphide to subside rapidly, leaving the supernatant liquid clear. Its contents were then filtered on a weighed filter paper dried at 110° C. The precipitate was washed with water until a few drops of the filtrate gave no reaction for chlorine with nitrate of silver, and then, in regular order, six times with alcohol, four times with bisulphide of carbon, and again four times with alcohol. I used the pump in all cases. The drying was done at 110° C. and to constant weight. Two hours invariably proved sufficient.

	Taken.	Calculated.	Found.
I.	20 cc. $\frac{N}{10}$ H_3AsO_4	0.1550 gram As_2S_5 = 0.0750 " As	0.1555 gram As_2S_5 = 0.0752 " As.
II.	30 cc. $\frac{N}{10}$ H_3AsO_4	0.2325 gram As_2S_5 = 0.1125 " As	0.2330 gram As_2S_5 = 0.1127 " As.
III.	50 cc. $\frac{N}{10}$ H_3AsO_4	0.3875 gram As_2S_5 = 0.1875 " As	0.3871 gram As_2S_5 = 0.1873 " As.
IV.	50 cc. $\frac{N}{10}$ H_3AsO_4	0.3875 gram As_2S_5 = 0.1875 " As	0.3879 gram As_2S_5 = 0.1877 " As.
V.	50 cc. $\frac{N}{10}$ H_3AsO_4	0.3875 gram As_2S_5 = 0.1875 " As	0.3875 gram As_2S_5 = 0.1875 " As.
VI.	50 cc. $\frac{N}{10}$ H_3AsO_4	0.3875 gram As_2S_5 = 0.1875 " As	0.3870 gram As_2S_5 = 0.1872 " As.

To see whether the trisulphide, when heated under pressure and in the presence of excess of sulphuretted hydrogen and a little air, could be made to take up sulphur and pass partially into the state of pentasulphide, I made the following experiment:[1]

50 cc. $\frac{N}{10}$ arsenious acid were brought into the bottle, strongly acidified with hydrochloric acid, and saturated with sulphuretted

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[1] It seemed possible that with the aid of the air remaining in the bottle the pentasulphide might be formed in accordance with the equation $As_2S_3 + 2H_2S + 2O = As_2S_5 + 2(H_2O)$.

hydrogen. Yellow trisulphide of arsenic was of course immediately precipitated. The bottle was closed and the whole heated in the boiling water-bath for one hour. I obtained, after filtering, washing, etc., 0.3095 gram As_2S_3 = 0.1887 gram As, whereas theory demands 0.1875 gram. The result is a trifle high, it is true, but the experiment certainly proves that no pentasulphide can be formed by heating together the trisulphide, sulphuretted hydrogen and *small* quantities of air.

To avoid the use of alcohol and carbon bisulphide in washing the precipitate, I proceeded as follows, and, as will be seen, with complete success:

B. The solution, after having been brought into the bottle and acidified with hydrochloric acid, was diluted with freshly boiled water until the bottle was nearly full, and then saturated with sulphuretted hydrogen. By so doing almost all the air was expelled from the bottle, and a subsequent separation of sulphur from the sulphuretted hydrogen by the action of any free oxygen rendered next to impossible.

The rest of the process was then conducted exactly as has been already described. The sulphide was washed with water until the filtrate was free from chlorine. I found it well, in order to promote the subsequent drying of the precipitate, to replace the water adhering to the same by running a small quantity of alcohol through the filter. This, however, is not necessary.

	Taken.	Calculated.	Found.
I.	25 cc. standard	0.2670 gram As_2S_5	0.2675 gram As_2S_5
	H_2KAsO_4	= 0.1292 " As	= 0.1294 " As.
II.	25 cc. standard	0.2670 gram As_2S_5	0.2671 gram As_2S_5
	H_2KAsO_4	= 0.1292 " As	= 0.1292 " As.
III.	25 cc. standard	0.2670 gram As_2S_5	0.2670 gram As_2S_5
	H_2KAsO_4	= 0.1292 " As	= 0.1291 " As.
IV.	50 cc. standard	0.5340 gram As_2S_5	0.5350 gram As_2S_5
	H_2KAsO_4	= 0.2584 " As	= 0.2588 " As.
V.	50 cc. standard	0.5340 gram As_2S_5	0.5331 gram As_2S_5
	H_2KAsO_4	= 0.2584 " As	= 0.2580 " As.
VI.	50 cc. standard	0.5340 gram As_2S_5	0.5333 gram As_2S_5
	H_2KAsO_4	= 0.2584 " As	= 0.2581 " As.
VII.	50 cc. standard	0.5340 gram As_2S_5	0.5335 gram As_2S_5
	H_2KAsO_4	= 0.2584 " As	= 0.2582 " As.
VIII.	50 cc. standard	0.5340 gram As_2S_5	0.5351 gram As_2S_5
	H_2KAsO_4	= 0.2584 " As	= 0.2588 " As.

50 cc. of this standard solution were precipitated under pressure and washed according to the first method, *i. e.* with water, until the filtrate was free from chlorine, then six times with alcohol, four times with bisulphide of carbon, and again three times with alcohol. I obtained 0.5326 gram $As_2S_5 = 0.2578$ gram As. The weight of the sulphide is somewhat below the required figure, but the corresponding amount of arsenic differs from the calculated quantity by only 0.0006 gram. It seemed well to analyse this standard solution by precipitating and weighing the arsenic as the trisulphide.

To do so, I reduced 50 cc. by heating the same with sulphurous acid under pressure, boiled off the sulphurous acid remaining, and precipitated the arsenic with sulphuretted hydrogen. The precipitate was carefully filtered, washed and dried according to Bunsen's directions. I obtained 0.4237 gram $As_2S_3 = 0.2583$ gram As. The amount required is 0.2584 gram As.

To further test this method of determining arsenic, I had a friend make up a solution of arseniate of potassium, such that every 50 cc. contained between 0.1 and 0.3 gram of arsenic. I made two analyses of this solution and obtained (1) 0.1336 gram As, and (2) 0.1331 gram As. The first precipitate was washed as Bunsen directs, the second according to my own method. The calculated result, as I was informed, was 0.1344 gram As. The salt, however, is not absolutely pure, as I have convinced myself by frequent and careful analysis. Allowing for the small amount of impurity, it will be seen that the agreement between the calculated quantity and the results found is entirely satisfactory.

I suggest, then, that when occasion arises for making an estimation of arsenic according to Bunsen's method, the modification here discussed be used. The process is a great improvement upon the Bunsen mode of procedure, for the following reasons: 1. It is remarkably rapid; 2. the quantity of sulphuretted hydrogen necessary for precipitation is reduced to a minimum; 3. no alcohol nor bisulphide of carbon is necessary for washing; and 4. the pentasulphide does not stick to the sides of the bottle, but separates out in such a state that every trace can be removed without even the aid of a feather.

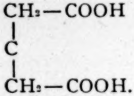
JOHN C. GREEN SCHOOL OF SCIENCE,
PRINCETON, N. J., *April* 1, 1887.

RESEARCHES ON ALLOISOMERISM.

I.

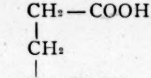
By Arthur Michael.

There is scarcely a subject in organic chemistry that has attracted more attention and has been more fully investigated than the isomerism of maleic and fumaric, and citra-, ita- and mesaconic acids. The interest shown in the examination of these acids has been largely due to the difficulty that the present theories of structural chemistry find in giving a satisfactory explanation of their constitution. Kekulé,[1] whose brilliant investigation of these acids may be considered as forming the corner-stone of our knowledge of their structure, made an attempt at an explanation, but it can hardly be considered as throwing much light on the subject. It was next considered by H. Kolbe, who in this, as in all other questions relating to isomerism and constitution of organic compounds, showed the keenest insight of any chemist of his time. Kolbe gave maleic and fumaric acids substantially the constitutions at present generally adopted.[2] Somewhat later, Kekulé[3] returned to the subject, and assigned analogous constitutions to the methyl homologues:



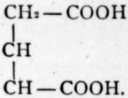
$$\begin{array}{l} CH_2-COOH \\ | \\ C \\ | \\ CH_2-COOH. \end{array}$$

Itaconic acid.



$$\begin{array}{l} CH_2-COOH \\ | \\ CH_2 \\ | \\ =C-COOH. \end{array}$$

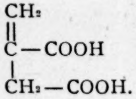
Citraconic acid.



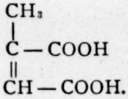
$$\begin{array}{l} CH_2-COOH \\ | \\ CH \\ | \\ CH-COOH. \end{array}$$

Mesaconic acid.

The formulæ of the first two acids were changed by Meilly,[4] in accordance with a better knowledge of the constitution of pyrotartaric acid, to the following:



$$\begin{array}{l} CH_2 \\ \| \\ C-COOH \\ | \\ CH_2-COOH. \end{array}$$



$$\begin{array}{l} CH_3 \\ | \\ C-COOH \\ \| \\ CH-COOH. \end{array}$$

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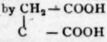
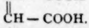
[1] Annalen der Chemie, Suppl. **2**, 114.

[2] Lehrbuch, 1ste Aufl. **2**, 579. Changed in accordance with the present notation, they are represented by



$$\begin{array}{l} CH_2-COOH \\ | \\ C\ \ -COOH \end{array}$$

and



$$\begin{array}{l} CH-COOH \\ \| \\ CH-COOH. \end{array}$$

[3] Zeitschrift für Chemie, N. F. **3**, 652.

[4] Annalen der Chemie **171**, 153.

To explain the isomerism of mesaconic acid, Henry[1] and Markownikoff[2] supposed it to be a polymeride of citraconic acid; a view, as Fittig has remarked, that can hardly be upheld, as Hübner and Schreiber[3] had shown that the evidently analogously constituted fumaric and maleic acids have the same molecular weight. Van't Hoff[4] deserves the credit of considering the subject from a new point of view. In his pamphlet on the constitution of organic substances he concluded that the isomerism of maleic and fumaric, and of citraconic and mesaconic, acids cannot be represented by the present views on the molecular constitution of organic compounds, and attempted to show that it may be explained by his ingenious hypothesis concerning the configuration of the molecule in space. This chemist suggested that several other knotty problems of organic chemistry may be explained in the same manner; as the constitution of the two β-chlorcrotonic and bromcinnamic acids, as well as those of angelic and tiglinic acids. It is perhaps because van't Hoff made no experimental contribution to the question, and the adopted structural theories permitted what seemed to most chemists a more plausible explanation of these cases of isomerism than that proposed by him, that his views were not adopted. The question was then made by Fittig[5] and his pupils the subject of an elaborate series of investigations. Fittig revived the formulæ of fumaric and maleic acids suggested by Kolbe, and believed that his work confirmed them. He followed a suggestion previously made by Kekulé, which is, that compounds containing a bivalent carbon should form addition products with more readiness than those containing so-called doubly-linked carbons. He showed that Kekulé's previous observation of the greater facility with which maleic and citraconic acids go over into saturated compounds than their isomerides is true in other reactions. These views seem to have been adopted by the majority of chemists, although it was known that a great many organic compounds containing so-called double bonds form addition products with equal facility; indeed, Anschütz[6] has shown that fumaric ether takes up bromine with as great readiness as any maleic compound; and they are evidently based on that curious dogma of double bonds, of the existence of which there is not a tittle of satisfactory proof. Finally, as to the latest contributions on the subject I refer to Kekulé and Anschütz's[1] hypothesis that fumaric acid consists of a right and left-handed optically active maleic acid; to Le Bel's[2] geometrical formulæ; to Erlenmeyer's[3] chemical explanation, and to a brief discussion of these and other views on the subject by the writer.[4]

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[1] Bull. Soc. Chim. **23**, 347.

[2] Annalen der Chemie **182**, 353.

[3] Zeitschrift für Chemie, N. F. **7**, 712.

[4] La Chimie dans l'Espace.

[5] Annalen der Chemie **188**, 95; **195**, 128, 169; **200**, 87.

[6] Berichte der deutschen chemischen Gesellschaft **13**, 1541.

It seemed as if contributions to our knowledge of this intricate case of isomerism might be made in two directions. In the first place, a more exact and general method of distinguishing between acids belonging to the fumaric and maleic acid series was desirable. The present means of distinction, which rests on the capability of the acid of forming an anhydride, means that the operation must be performed at a temperature where intramolecular changes are not unlikely to occur, that a comparatively large amount of the acid must be used, and it is not applicable to a large number of unsaturated acids, the classification of which would doubtless throw light on the constitution of the already classified acids; secondly, an examination of such unsaturated halogen acids as the so-called β-chlor- and β-isochlorcrotonic, and α- and β-bromcinnamic acids, with a view of bringing indisputable proofs in regard to their constitutions. The present views on the constitution of organic compounds seem to many chemists to represent a state of finality, instead of being only a guide to a better insight; and this is probably the reason why the constitution of so many compounds is accepted without any further proof, simply because their existence is indicated by the present hypotheses. In no part of organic chemistry is this more noticeable than among unsaturated acids and their halogen derivatives, where the constitution of many compounds has been assigned in apparent contradiction to all analogy, simply that their existence may be explained by the present views on chemical isomerism.

A clue to a general method of distinguishing between acids of the fumaric and maleic series was found in an observation made by Gottlieb,[5] that an aqueous solution of the aniline salt of citraconic acid gives citraconanil on boiling, while a solution of the isomeric aniline mesaconate can be evaporated to dryness without undergoing a change. On following this line of investigation, it was found that the distinction is general between acids of the fumaric and maleic series, and the results obtained form the subject of the following communications.

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[1] Berichte **14**, 717; **18**, 1400.

[2] Bull. Soc. chim. **37**, 300.

[3] Berichte der deutschen chemischen Gesellschaft **19**, 1937.

[4] *Ibid.* **19**, 1381; **20**, 554.

[5] Annalen der Chemie **77**, 277.

I.—A RELATION BETWEEN THE CONSTITUTION OF POLYBASIC UNSATURATED ORGANIC ACIDS AND THE FORMATION OF THEIR ANILIDES.

BY ARTHUR MICHAEL.

Behavior of Maleic Acid towards Aniline.

To a solution of 8 grams of maleic anhydride (1 mol.) in 100 grams of water 7.4 grams of aniline (1 mol.) were added. The aniline went immediately into solution, which was then heated in a water-bath, when presently needles began to separate. After heating for an hour, the contents of the flask were allowed to cool, filtered, and the filtrate heated again, when it gave a further deposit of needles on cooling. The substance was purified by several crystallisations from alcohol, and gave on analysis the following result:

0.2314 gram substance gave 0.6115 gram CO_2 and 0.1145 gram H_2O.

	Theory for $\begin{array}{l} CH-CONHC_6H_5 \\ \vert \\ CH-CONHC_6H_5. \end{array}$	Found.
C	72.18	72.07
H	5.26	5.49

The anilide crystallises from alcohol in long white needles that melt at 211°-212°. It is somewhat soluble in hot, sparingly in cold water; readily in hot, pretty soluble in cold alcohol. It is insoluble in dilute mineral acids and alkalies. The formation of the anilide may be represented as follows:

$$\begin{array}{l} CH-COONH_3C_6H_5 \\ \vert \\ CH-COONH_3C_6H_5 \end{array} = \begin{array}{l} CH-CONHC_6H_5 \\ \vert \\ CH-CONHC_6H_5 \end{array} + 2H_2O.$$

Besides the dianilide of maleic acid, a second substance, which remains in the alcoholic mother liquor, is formed in the reaction. This compound is insoluble in dilute acids and alkalies, and may represent the anil.[1] [2]

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[1] I have lately noticed that W. H. Perkin observed the formation of anilides from aqueous aniline maleate about six years ago (Berichte **14**, 2540), and also that aniline fumarate remains unchanged. He made no analyses, and did not follow up the experiments.

[2] This paper, including the note referring to Perkin's observations, was in the hands of the printer when I received a paper by Anschütz and Wirtz (Annalen der Chemie **239**, 137) on the

Behavior of Fumaric Acid towards Aniline.

A dilute aqueous solution containing fumaric acid and aniline, in proportion to form the acid aniline salt, was heated for several days in a flask connected with an upright cooler. No precipitate was formed under these conditions, neither did anything separate from the solution on cooling. It contained unchanged aniline fumarate, and gave a precipitate of fumaric acid on addition of chlorhydric acid. This experiment was repeated with the same result with a concentrated solution of the salt, as well as when aniline in proportion to form the neutral aniline salt was used. If an aqueous solution of acid aniline fumarate is concentrated in an evaporating dish, it will be noticed that towards the end of the operation a precipitate is deposited. This consists of fumaric acid, as both the acid and neutral aniline salts of fumaric acid, when boiled with water, gradually decompose into acid and free base, the latter passing off with the steam.

anilides of fumaric and maleic acids. These chemists have made a detailed investigation of the substance designated as the dianilide of maleic acid, and find that it gives phenylaspartic acid when treated with acids or alkalies. In view of these observations they change the constitution of the anilide to that of the isomeric anil of phenylaspartic acid. The constitution I assigned to the compound was the only one that could be given it at the time of the experiment.

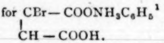
I take this opportunity to explain the mistakes that led Mr. Wing and myself (This Journal **7**, 282) to give the constitution of a fumaric dianilide to the anil of maleic acid. A nitrogen estimation (owing to an erratum .1484 gram of substance was printed instead of .1984 gram) gave 10.19 per cent., a result that agrees fairly well with the amount indicated by theory. A carbon and hydrogen analysis gave 69.24 C and 4.30 H. This analysis was rejected, as everything seemed to point to the impossibility of the substance being an anil. It gave fumaric acid on continued boiling with water, and as there was no ground for supposing the existence of an anil of fumaric acid, the only explanation would have been the conversion of a maleic derivative into fumaric acid by heating with water, which seems very improbable. In the second analysis Mr. Wing made the mistake of adding the increase of weight of the solid caustic potash twice, and thereby got results that agreed with those indicated by the dianilide. Anschütz and Wirtz seem to have overlooked our statement that the compound is decomposed by continued boiling with water into fumaric acid and aniline, and give the existence of the supposed dianilide of maleic acid as a reason for our believing the compound to be an anilide of fumaric acid; but, as the empirical constitution of the maleic derivative was unknown at the time, it is not likely that this could have entered into our calculations.

Perkin's observation on the formation of the anil of phenylaspartic acid differs from mine, as he heated the dry product to 100°, while I have made a point of showing the anilide formation in the presence of water in my experiments. The fact that an anilide is not formed from aniline mesaconate had already been noticed by Gottlieb, and the formation of citraconanil from a cold solution of aniline citraconate would seem, judging from the observations mentioned in the following paper, to be a mistake. As already stated, Perkin made no analyses, nor did he follow up his observations, and his opinion in regard to the constitution of the maleic acid derivative was based solely on the fact that aniline citraconate under the same conditions gives citraconanil. In view of this it is not a little surprising that Anschütz and Wirtz should endeavor to convey the impression that the views of Perkin and myself on the constitution of the substance conflicted. It would seem as if advantage was taken of circumstances to convey to the reader what seems to me to be almost a misrepresentation of the actual state of affairs.

Behavior of Monobrommaleic Acid towards Aniline.

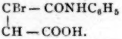
Monobrommaleic acid (obtained from dibromsuccinic acid by boiling with water, and melting at 128°) was dissolved in about seven parts of water, and an equivalent quantity of aniline added. The base dissolved, and presently a crystalline precipitate separated. This consisted of clusters of plates, melting at 128°–128½°, soluble in dilute chlorhydric acid. They are the acid aniline salt.

0.2592 gram salt gave 0.1665 gram AgBr.

	Theory for  $\begin{array}{l}CBr-COONH_3C_6H_5\\ \vert \\ CH-COOH.\end{array}$[1]	Found.
Br	27.75	27.30

If this acid salt is dissolved in water, and the solution allowed to stand several days at ordinary temperature, it will be noticed that a crystalline substance gradually separates.

0.2472 gram gave 0.1708 gram AgBr.

	Theory for  $\begin{array}{l}CBr-CONHC_6H_5\\ \vert \\ CH-COOH.\end{array}$	Found.
Br	29.63	29.36

The compound is the acid anilide of brommaleic acid, and crystallises in prisms. It is insoluble in dilute chlorhydric acid.

The action of aniline on brommaleic acid in the heat gives entirely different results from those obtained by allowing the reaction to proceed in the cold. The solution, on boiling, soon turns yellow, and a crystalline substance begins to separate. This substance is best made by heating a solution of the neutral aniline salt in about thirty parts of water, in a flask connected with an upright condenser, to boiling for about twenty minutes, and filtering the liquid while hot. The yellow precipitate was purified by several crystallisations from alcohol, and was found to be free of bromine.

0.2055 gram substance dried at 100° gave 0.5513 gram CO_2 and 0.0839 gram H_2O.

	Theory for $C_{16}H_{12}N_2O_3$.	Found.
C	72.73	73.10
H	4.55	4.62

The substance crystallises from alcohol as ochre-colored, round clusters of microscopic needles that melt at 229°–230°. It is moderately soluble in hot, sparingly in cold water; in hot alcohol it is pretty soluble, less in cold. The substance is insoluble in dilute acids and alkalies, but on standing with dilute solutions of the last reagent it very slowly goes into solution, to form the salt of a different substance, which is precipitated on addition of acids; a result that takes place much more rapidly if warm alkali is used.

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[1] In this, and in a number of other constitutions, it is assumed that the base will unite with the carboxyl of the acid that is most under the influence of negative radicals.

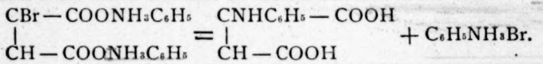
The aqueous filtrate from the yellow needles deposits a second substance, mixed with some of the first, on cooling. To separate these substances they may be crystallised from a small amount of water, filtering off the insoluble portion. It is easier, however, to treat the mixture with a very dilute solution of caustic alkali, which dissolves the new substance, leaving the yellow needles behind. The filtrate was carefully neutralised, and the precipitate purified by crystallisation from alcohol. It does not contain bromine.

0.2153 gram substance dried at 100° gave 0.5389 gram CO_2 and 0.102 gram H_2O.

	Theory for $C_{16}H_{14}N_2O_3$.	Found.
C	68.09	68.23
H	4.96	5.27

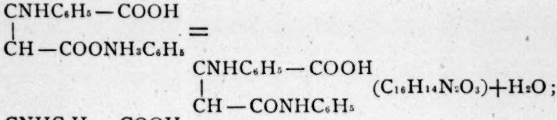
The substance separates from water as very slightly yellow-colored, round groups of indistinct small crystals that melt at 176°. It is quite soluble in hot, moderately in cold water. Alkalies dissolve it immediately, and the addition of an acid causes a precipitate of the unchanged substance.

These substances stand in a simple relation to phenyl-amidomaleic acid, a substance that may be supposed to be the first product of the action of aniline on brommaleic acid in the heat:

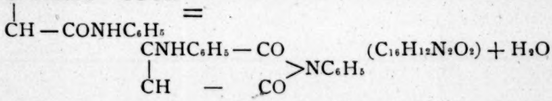


$$\begin{array}{l}CBr-COONH_3C_6H_5\\ |\\ CH-COONH_3C_6H_5\end{array} = \begin{array}{l}CNHC_6H_5-COOH\\ |\\ CH-COOH\end{array} + C_6H_5NH_3Br.$$

This acid unites with aniline to form a salt, and, being under conditions that make the existence of an aniline salt of a derivative of maleic acid impossible, a condensation takes place:



$$\begin{array}{l}CNHC_6H_5-COOH\\ |\\ CH-COONH_3C_6H_5\end{array} = \begin{array}{l}CNHC_6H_5-COOH\\ |\\ CH-CONHC_6H_5\end{array} (C_{16}H_{14}N_2O_3)+H_2O;$$



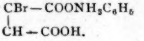
$$\begin{array}{l}CNHC_6H_5-COOH\\ |\\ CH-CONHC_6H_5\end{array} = \left.\begin{array}{l}CNHC_6H_5-CO\\ |\\ CH\quad-\quad CO\end{array}\right>NC_6H_5 \quad (C_{16}H_{12}N_2O_2)+H_2O$$

The bright yellow substance, according to this interpretation, is the anil of phenyl-amido-maleic acid, and the pale yellow compound an acid anilide of the same acid.[1]

Behavior of Bromfumaric Acid towards Aniline.

Monobromfumaric acid (melting point 177°–178°: made by heating dibromsuccinic acid and water to 150° in a sealed tube, and also by treating brommaleic with fuming bromhydric acid) and aniline in equivalent proportions unite immediately to form the acid aniline salt. This salt is quite insoluble in water, much more so than the corresponding brommaleic acid salt, and by adding aniline to a solution of one part of acid in thirty of water, a copious precipitate soon separates. For analysis it was crystallised from water. It melts at 153°–154°, and is soluble in dilute chlorhydric acid.

0.2697 gram salt gave 0.1750 gram AgBr.



	Theory for $\begin{array}{l}\mathrm{CBr-COONH_3C_6H_5}\\ \mid\\ \mathrm{CH-COOH.}\end{array}$	Found.
Br	27.75	27.53

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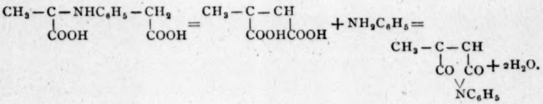
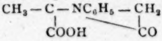
[1] Shortly after a preliminary note on this work (Berichte **19**, 1376) was sent to the German Chemical Gazette for publication, I received Part No. 6 of the journal that contained a paper by Reissert and Tiemann (**19**, 626). These chemists had examined the action of aniline on dibromsuccinic acid, and obtained two compounds that are identical with the products obtained from the halogen fumaric and maleic acids. Reissert and Tiemann considered it probable that the anil represented a dipyridylene, but adopted the view presented in my preliminary note after its publication (Reissert, *ibid.* **19**, 1644). I should like to call attention to the constitution of the condensation products of phenyl-amido-pyrotartaric acid, which Tiemann and Reissert have classified as quinoline derivatives. Although they (*Ibid.* **19**, 624) mention that the compounds have the composition of methyl-fumaranilic acid and methyl-fumaranil, they reject the interpretation that their compounds are really the ones named; but their pyranilpyroinic anhydride has the melting point of citraconanil (98°), and all the properties of that compound. Its formation is very readily understood when we bear in mind that β-amido acids have a tendency to decompose into unsaturated acids and bases, as is shown in the decomposition of β-amido-propionic acid into acrylic acid and ammonia. The formation of citraconanil from phenyl-amido-pyrotartaric acid may be represented by the following equations:



$$\mathrm{CH_3-\underset{\substack{\mid\\ COOH}}{C}-NHC_6H_5-\underset{\substack{\mid\\ COOH}}{CH_2}} = \mathrm{CH_3-\underset{\substack{\mid\\ COOH}}{C}-\underset{\substack{\mid\\ COOH}}{CH}} + \mathrm{NH_2C_6H_5} = \begin{array}{c}\mathrm{CH_3-C-CH}\\ \quad\mid\quad\ \mid\\ \quad\mathrm{CO\ \ CO}\\ \quad\diagdown\diagup\\ \quad\mathrm{NC_6H_5}\end{array} + \mathrm{2H_2O.}$$

If, as Tiemann and Reissert assert, the so-called pyranilpyroinic acid is formed from citraconanil by alkalies, then this acid is citraconanilic acid; although the melting point of that acid is 175°, and these chemists give 165° for their product. Perhaps a more detailed investigation will disclose the identity of citraconanilic acid with the acid obtained from their so-called anhydride; and if the first condensation product should turn out not to be citraconanilic acid, it doubtless has the constitution $\mathrm{CH_3-\underset{\substack{\mid\\ COOH}}{C}-NC_6H_5-\underset{\substack{\mid\\ CO}}{CH_2}}$

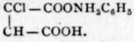


This salt shows a much greater stability than the corresponding brommaleic derivative. It may be allowed to stand with water for weeks without undergoing a change, and its solution in water does not give, on long standing, a precipitate of an anilide. If a solution of the salt is boiled for about ten minutes, a yellow precipitate begins to form, which becomes quite copious on long boiling. The solution, after boiling about an hour, was filtered hot, and the yellow precipitate crystallised several times from alcohol. The substance melted at 229°-230°, and agreed in its properties with the yellow substance obtained by heating a solution of aniline brommaleate. In order to explain its formation it is necessary to assume that phenyl-amido-fumaric acid at the temperature of boiling water changes into the alloisomeric phenyl-amido-maleic acid, which in the presence of aniline decomposes into the anil.

Behavior of Chlorfumaric Acid towards Aniline.

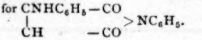
Five grams of monochlorfumaric acid (melting point 183°: obtained by the action of phosphorus pentachloride on tartaric acid) were dissolved in one hundred grams of water, and two and one-half grams of aniline added. The aniline went into solution, and presently a crystalline substance separated. For analysis it was crystallised twice from alcohol.

0.2736 gram air-dried substance gave 0.1610 gram AgCl.

	Theory for  $\begin{array}{l}CCl-COONH_3C_6H_5\\ \vert\\ CH-COOH.\end{array}$	Found.
Cl	14.57	14.55

Acid aniline chlorfumarate crystallises from alcohol as white monoclinic prisms with domes, that melt at 178°, but begin to turn yellow at about 170°. It is difficultly soluble in cold water and alcohol, but readily in chlorhydric acid, when it decomposes into chlorfumaric acid and aniline chlorhydrate. This salt or its aqueous solution may be allowed to stand for weeks with water without undergoing any change. An aqueous solution of the salt behaves on boiling like the corresponding bromfumaric acid salt; only its conversion into the anil of phenyl-amido-maleic acid proceeds with less readiness. When a solution of the salt is boiled a number of minutes, the unchanged salt is deposited on cooling. If the boiling is continued for some time the solution gradually turns yellow, and the yellow anil begins to separate. This was purified as already described, and gave the same compound as obtained from brommaleic and bromfumaric acids.

0.1573 gram substance gave 0.4195 gram CO_2 and 0.0677 gram H_2O.



$$\begin{matrix}\mathrm{CNHC_6H_5-CO} & \\ \mid & >\mathrm{NC_6H_5.} \\ \mathrm{CH}\quad\;\; \mathrm{-CO} & \end{matrix}$$

	Theory for $\mathrm{CNHC_6H_5-CO}$ / $\mathrm{CH-CO} > \mathrm{NC_6H_5}$.	Found.
C	72.73	72.76
H	4.55	4.79

The formation of the same compound from brommaleic, brom- and chlorfumaric acids when aqueous solutions of their neutral aniline salts are boiled is of considerable theoretical importance, as it implies the conversion of derivatives of fumaric acid into a maleic acid compound at the temperature of boiling water, a fact that can only be brought in harmony with Fittig's views of the constitution of these compounds with the assumption of improbable intermolecular changes. I shall return to the subject in a discussion of the bearings of the present investigation on the constitution of the acids in question.

Behavior of Dibrommaleic Acid towards Aniline.

This reaction is complicated, and, according to the conditions of the experiment, a number of different products are formed, which, however, are difficult to obtain in a pure state.

To a solution of the acid in thirty parts of water an equivalent proportion of aniline was added. The base dissolved, and immediately the very difficultly soluble acid aniline dibrommaleate was deposited. This salt dissolves in dilute chlorhydric acid, to form the free acid and aniline chlorhydrate. If it is allowed to stand under water for a number of days it gradually loses water to form an anilide, which decomposes when heated with water or other solvents, and could not be obtained in a state suitable for analysis. The neutral salt, formed on adding two equivalents of aniline to a solution of one of the acid, is also quite insoluble. It dissolves in dilute chlorhydric acid. When allowed to stand under water for a long time it also passes over into an anilide that may be separated from any unchanged salt by treating with dilute chlorhydric acid. This salt when heated in a solvent goes over into a mixture of a yellow substance that is described further on, and unchanged substance. As it was found impossible to crystallise the substance without its undergoing a partial change, it was dried in a vacuum and analysed.

0.2224 gram substance gave 0.2041 gram AgBr.

	Theory for $\begin{array}{l}CBr-CONHC_6H_5\\ \,|\\ CBr-CONHC_6H_5.\end{array}$	Found.
Br	37.73	38.98

The substance probably contained a small amount of the anil, but the analysis is sufficiently close to show that the product analysed consisted largely of the dianilide. It was obtained as plates that melted at 138°–140°. The anil is probably obtained by crystallising the anilide, obtained from the acid aniline salt, from ligroin. The solution, on cooling, deposited large white plates, but as they were mixed with yellow needles, and as no satisfactory way could be found to separate the two compounds, no analyses were made. It melts at 160°–162°, and is insoluble in dilute chlorhydric acid.

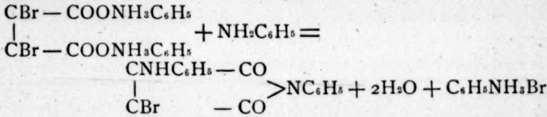
The yellow compound may be obtained in a pure state by heating three parts of acid in sixty parts of water and 2.2 parts of base for about half an hour, and filtering hot from the reddish yellow precipitate. This was extracted with a small amount of hot alcohol that dissolves some of the substance and most of the dark impurities. The residue was purified by three crystallisations from hot alcohol.

0.1949 gram substance dried at 100° gave 0.1066 gram AgBr.

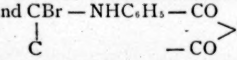
0.2285 gram substance dried at 100° gave 0.1260 gram AgBr.

	Theory for $\begin{array}{l}CNHC_6H_5-CO\\ \,|\\ CBr\qquad\;\, -CO\end{array}\!\!>NC_6H_5.$	Found.	
Br	23.29	23.32	23.46

The anil crystallises from alcohol as flat prisms with end-faces generally at right angles, but in some crystals they obliquely truncated the sides. They melt (under decomposition) at 182°–183°. When large the crystals have a reddish yellow color, but as a powder or as very small crystals it is almost pure yellow. They are insoluble in hot water, and only moderately soluble in hot alcohol. Dilute chlorhydric acid and dilute alkalies do not dissolve them.



$$\begin{array}{l}CBr-COONH_3C_6H_5\\ \,|\\ CBr-COONH_3C_6H_5\end{array} + NH_2C_6H_5 = \begin{array}{l}CNHC_6H_5-CO\\ \,|\\ CBr\qquad\;\; -CO\end{array}\!\!>NC_6H_5 + 2H_2O + C_6H_5NH_3Br.$$

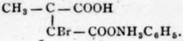
The formation of this substance is of interest because it shows that dibrommaleic acid can hardly have the commonly accepted constitution. If both the bromine atoms were united with the same carbon there is every reason for supposing that a substance free of halogen would have resulted from the reaction, as the compound  $\begin{array}{l} CBr-NHC_6H_5-CO \\ \; | \\ C \qquad\qquad\quad -CO \end{array}\!>NC_6H_5$ would, judging from what we know of the properties of this class of substances, hardly show the stability of the substance in question, but would decompose into a substance free of halogen and bromhydric acid.

A substance free of halogen and crystallising as dark red plates may be obtained by heating the acid in aqueous solution with a large excess of aniline. I did not succeed, however, in getting it into a state suitable for analysis.

Behavior of Bromcitraconic Acid towards Aniline.

Bromcitraconic anhydride (melting point 99°–100°) was dissolved in twenty parts of water, and an equivalent of aniline added to the solution. The base dissolved and a crystalline precipitate was immediately deposited. This substance was filtered, washed with water, and analysed.

0.2461 gram substance dried in vacuum gave 0.1556 gram AgBr.

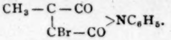
Theory for  $\begin{array}{l} CH_3-C-COOH \\ \quad\; | \\ \quad CBr-COONH_3C_6H_5. \end{array}$

	Theory	Found.
Br	26.91	26.50

The acid aniline bromcitraconate crystallises in clusters of small white rhombic plates that melt at 120°–121°, turning yellow. It is soluble in dilute chlorhydric acid, but careful neutralisation of the solution with ammonia throws down the original substance. It is somewhat soluble in cold water.

If this salt is allowed to stand under water for a few hours, or its solution in water heated for a minute, it passes over into the anil.[1] The substance was purified by crystallisation from alcohol.

0.2630 gram substance dried at 100° gave 0.1871 gram AgBr.
0.3071 " " " " " " 0.2197 " "

Theory for  $\begin{array}{l} CH_3-C-CO \\ \quad\; | \\ \quad CBr-CO \end{array}\!>NC_6H_5.$

	Theory	Found.	
Br	30.07	30.26	30.41

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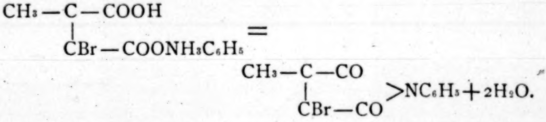
[1] Through a mistake on my part this substance was represented as the acid anilide in the preliminary note, Berichte **19**, 1373.

It crystallises in stellar groups of prismatic needles that melt at 144.5°–145.5°, and are insoluble in cold, slightly in warm water. They are readily soluble in hot, moderately in cold alcohol, and are insoluble in dilute chlorhydric acid.



$$\begin{array}{l} CH_3-C-COOH \\ \quad\;| \\ \quad CBr-COONH_3C_6H_5 \end{array} = \begin{array}{l} CH_3-C-CO \\ \quad\;| \\ \quad CBr-CO \end{array}\!\!>NC_6H_5+2H_2O.$$

Behavior of Aconitic Acid towards Aniline.

The importance of the aniline reaction for ascertaining whether an unsaturated polybasic organic acid belongs to the maleic or fumaric acid series is shown when the classification of acids like aconitic, which decompose into simpler products on heating, is in question. That the method based on the formation of anhydrides cannot be used in such cases is obvious; but, as the following experiments indicate, the behavior of an aqueous solution of the aniline salts of such acids is adapted to show to which series they belong.

An aqueous solution of dianiline aconitate, when boiled in a flask connected with a condenser, soon deposits an oily substance, mixed with some yellow needles. After the formation of the precipitate ceased to increase, it was separated from the mother liquor and extracted with a little hot alcohol, which dissolved the amorphous substance. The residue was crystallised three times from alcohol.

0.1237 gram substance gave 0.323 gram CO_2 and 0.0545 gram H_2O.

	Theory for $C_{18}H_{14}N_2O_3$.	Found.
C	70.59	71.13
H	4.57	4.91

The substance crystallises in very light yellow fine needles that melt at 250°–252°.[1] It is insoluble in water, sparingly soluble in hot alcohol. The very small yield of this substance obtained did not permit further examination. It may be identical with the anilide obtained by Pebal[2] by heating aniline aconitate to 140°, as its properties agree with those of the compound obtained by that chemist. The amorphous mass that is the principal product of the reaction could not be brought into a crystalline form. It is insoluble in dilute chlorhydric acid, and is possibly an anilide of the acid.

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[1] In the preliminary note the melting point of a less pure product was given at 215°–217°.

[2] Annalen der Chemie **98**, 81.

Far better results were obtained by allowing an aqueous solution of the dianiline salt to remain for some time at ordinary temperature. An amorphous substance also separates in this instance, but in equal quantities a crystalline substance. To separate them the precipitate was extracted with cold alcohol, when most of the amorphous substance went into solution. The residue was then crystallised four times from alcohol.

0.2102 gram substance, dried at 100° C. in vacuum, gave 0.5134 gram CO_2 and 0.1028 gram H_2O.

0.3334 gram substance, dried at 100° C. in vacuum, gave 23 cc. N at 765.2 mm. and 19° C.

	Theory for $C_{18}H_{16}O_4N_2$.	Found.
C	66.69	66.60
H	4.94	5.43
N	8.64	8.15

The substance crystallises in long prismatic needles that have a very faint pinkish cast and melt at 188°–189°. They are insoluble in hot water and dilute chlorhydric acid, but dissolve in alkalies; in hot alcohol they are pretty soluble, moderately in the cold solvent. Strong chlorhydric acid dissolves the substance in the cold, but the addition of water to the solution gives a precipitate of the original substance. The substance is formed from the dianiline salt by elimination of two molecules of water.[1]

It is evident from these results that aconitic acid belongs to the maleic and not to the fumaric acid series.[2] I shall return to the importance of this conclusion in regard to the constitution of maleic acid in another paper.

Behavior of Citra- and Itaconic Acids towards Secondary and Tertiary Aromatic Amines.

According to an observation made by Gottlieb,[3] an aqueous solution of monoethyl-aniline citraconate can be evaporated to dryness, and the residue heated to melting, without undergoing a change. It will be shown in the following paper that all primary aromatic amines having basic properties give anilides when aqueous solutions of their citraconic acid salts are heated, and it seemed of interest to examine secondary and tertiary aromatic amines in their behavior towards the new reagent, as a convenient method of separation could probably be based on the results.

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[1] It would be premature to assign structural formulæ to these compounds, although it is very likely they stand in the relation of anilides to the acid. The formation of substances that are insoluble in dilute chlorhydric acid from aqueous solutions of the aniline salt is evidently sufficient to classify the acid as belonging to the maleic series. It is my intention, however, to have these compounds made the subject of a detailed examination.

[2] I have lately made some aconitic acid by heating the ether with strong chlorhydric acid in a sealed tube at 100°, when the pure acid separates on cooling. This product is quite insoluble in pure ether, while the acid obtained by heating citric acid is generally represented to be very soluble in that solvent. Is it possible that the first product represents the aconitic acid of the fumaric series? The subject deserves further investigation.

[3] Annalen der Chemie 77, 292.

A solution of the acid, as well as the neutral, monoethyl-aniline citraconate can be gently warmed without any change, but on boiling the solution it will be noticed that the base is readily given off; in fact, a dilute aqueous solution of these salts when boiled to dryness is free of base, and the residue contains nothing but citraconic acid. The formation of an anilide when the base was not allowed to escape was never noticed, although the boiling was continued for a long time and very concentrated solutions were used. It was noticed, however, that solutions of the salts which were clear in the cold gave, on warming, a deposit of methyl-aniline; a proof that the decomposition of the salts into base and acid takes place at the temperature of boiling water. Similar experiments were then made with monoethyl-aniline salts, and exactly the same results were obtained. A dilute aqueous solution of the salt when boiled down to dryness is free of base, and a solution made in the cold sets the base free when heated to 100°.[1]

The dimethyl- and diethyl-aniline salts of citraconic acid are probably represented by the solutions obtained by saturating a strong aqueous solution of citraconic acid with the bases in the cold, but these compounds are so unstable that dilution suffices to decompose them into base and acid, and by heating the mixtures the base volatilises readily with the steam.

The ethyl derivatives of paratoluidine behaved exactly like the corresponding aniline compounds towards citraconic acid.

To a solution of 2.4 grams of citraconic acid in 10 grams of water, 3.4 grams of diphenylamine were added, and the mixture was then boiled for an hour. On cooling the diphenylamine separated unchanged, and was completely soluble in dilute chlorhydric acid.

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[1] I am unable to explain the results obtained by Gottlieb with this salt, but suspect that he did not use pure ethylaniline, which, at the time of his experiments, was extremely difficult to obtain in a pure state.

As itaconic acid forms only an acid anilide with aniline, it was thought possible that this acid might give an anilide with monomethyl and ethyl-aniline, but experiments showed that it acts exactly like citraconic acid toward these bases.

On these results a method of detecting and separating primary aromatic amines from secondary and tertiary amines was based. It is only necessary to dissolve the basic mixture in a solution of citraconic acid, then add an equal volume of citraconic acid to the solution, and boil in a flask with a reversed cooler for several hours. The flask is then connected with a condenser and the contents rapidly distilled almost to dryness, when, if oil-drops still go over towards the end of the operation, more water is added, and the operation repeated. The residue in the flask contains all the primary amines as anilides, and the bases may be obtained as chlorhydrates by decomposing the precipitate with strong chlorhydric acid. If the mixture contains secondary and tertiary amines which are not volatile with steam, the precipitate is treated with dilute chlorhydric acid, when they dissolve, leaving the anilide unchanged. It is not unlikely that the method may be used for a quantitative separation. For detecting a primary aromatic amine a small amount is treated as above in a test-tube, the solution boiled several minutes, replacing the water if necessary, and cooled. If a precipitate is formed that does not completely dissolve in dilute chlorhydric acid, the presence of a primary base may be considered as proved.[1]

Behavior of Acetic and Succinic Acids towards Secondary and Tertiary Aromatic Bases.

The results obtained with citraconic acid were the reason for an examination of the behavior of acetic and succinic acids, as types of fatty mono- and dibasic acids, towards aromatic bases.

Glacial acetic acid and aniline, in equivalent proportions, form, at ordinary temperature, a clear solution of aniline acetate. If this solution is kept under 30° it remains perfectly clear, but above that temperature it begins to become turbid, owing to the separation of minute oil-drops. It increases in turbidity up to 50°, above which temperature it gradually becomes less turbid, and finally perfectly clear at about 60°. On cooling the solution these phenomena are reversed. This remarkable behavior is evidently due to the presence of a small amount of a base in so-called pure aniline, that has weaker basic properties than aniline itself. This view is corroborated by the following observation. If some water is added to aniline acetate the separation of a small amount of oil takes place, although the solution shows a strong acid reaction. The oil dissolves again when about three times as much water is added as the volume used of aniline acetate.[1]

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[1] It is evident that other unsaturated acids, as itaconic or phthalic acids, may be used. I have experimented with citraconic acid as it seemed best adapted for the purpose, and can be made in large quantities without trouble. It is also apparent that the reaction may be used for detecting acids belonging to the maleic acid series, and in some instances to separate them from other organic acids. With acids like citra-, itaconic, and phthalic, the separation is almost quantitative. There is no doubt that the reaction will prove of considerable use, not only in the investigation of basic aromatic mixtures, but also in studying the decomposition products of organic polybasic acids.

An aqueous solution of aniline acetate, when boiled gradually, decomposes, and at first free aniline passes off; after this, a distillate that remains clear on cooling, which, as it contains both base and acid, evidently is aqueous aniline acetate; and, finally, acetic acid. I have tried a number of aniline salts of volatile fatty acids, and believe that the relation just described may be considered as a general one.

Mono- and dimethyl-aniline, and also the ethyl derivatives, dissolve in the equivalent amount of glacial acetic acid; but it is a matter of doubt whether it is more than simple solution, as the addition of water causes the base to separate. On the differences in their behavior towards acetic acid a separation of primary amines from the secondary and tertiary bases was based. The basic mixture is dissolved in an excess of glacial acetic acid, three times the volume of water added, the mixture heated, and the oil separated from the solution of primary acetate. It is doubtful, however, whether this method is as exact as the one previously described.[2]

Succinic acid (6 grams) was dissolved in a small quantity of lukewarm water, and methylaniline (5 grams) added. On cooling, most of the base separated from the solution, which was filtered. The solution is clear at ordinary temperature, but becomes turbid, owing to the separation of an oil at about 30°. When boiled, methylaniline escapes, leaving a solution of pure acid.

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[1] It is doubtful whether perfectly pure aniline has ever been made. The oil may be amidothiophene, and its investigation is certainly of interest. I shall attempt to obtain it in sufficient amount to ascertain its nature.

[2] This method can of course only be used to separate those primary aromatic amines that form salts with acetic acid.

Behavior of Citraconic Acid towards Fatty Amines.

That the formation of anilides from primary aromatic bases and citraconic acid stands in a close relation to the comparatively weak basic properties of the substances is shown by the behavior of mono-, di- and triethyl-amine citraconates. The acid and neutral salts of these bases may be evaporated to dryness without undergoing any decomposition. A solution of amidoacetic acid in citraconic acid may be boiled without forming an anilide. On evaporating to dryness a residue soluble in water was obtained, but it is uncertain whether it was a citraconate or simply a mixture of the two substances. Aspartic acid does not combine with organic acids.[1]

II.—A RELATION BETWEEN THE CONSTITUTION OF POLYBASIC UNSATURATED ORGANIC ACIDS AND THE FORMATION OF THEIR ANILIDES.

BY A. MICHAEL AND G. M. PALMER.

Behavior of Maleic Acid towards Aniline.

It was shown in the preceding paper that an aqueous solution of aniline maleate, on boiling, gives maleic dianilide. A different result is obtained when a solution of acid aniline maleate in ten parts of water is allowed to stand in the cold. After standing a day a crystalline substance was deposited from the solution, which was filtered and the operation repeated until no further deposit is formed. The crystals were purified by repeated crystallisation from alcohol, and are the acid anilide of maleic acid.

0.1746 gram substance gave 0.4025 gram CO_2 and 0.0875 gram H_2O.

	Theory for $\begin{array}{l}CH-CONHC_6H_5\\ \vert\\ CH-COOH.\end{array}$	Found.
C	62.82	62.91
H	4.71	5.56

The anilide crystallises from dilute alcoholic solutions in almost white prismatic plates, from concentrated solution in plates whose end-faces are imperfectly developed. The crystals melt at 207°. It is soluble in hot water and alcohol, moderately in cold alcohol. Dilute chlorhydric acid does not dissolve it, but it is soluble in dilute aqueous alkalies. Its formation is represented thus :

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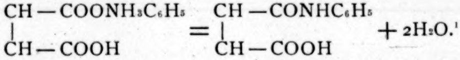
[1] The best method of making aspartic acid from asparagine is to boil that substance with alkalies until ammonia ceases to come off, and then acidulate with acetic acid, when all the aspartic acid is precipitated.



$$\begin{array}{l}CH-COONH_3C_6H_5\\ |\\ CH-COOH\end{array} = \begin{array}{l}CH-CONHC_6H_5\\ |\\ CH-COOH\end{array} + 2H_2O.$$[1]

Behavior of Citraconic Acid towards Aniline.

An aqueous solution of mono-aniline citraconate behaves like the maleic acid compound, when it is allowed to stand in the cold. The solution deposits more or less rapidly, according to its dilution, large white crystals, which were crystallised from alcohol.

0.3175 gram substance gave 0.7531 gram CO_2 and 0.1532 gram H_2O.

	Theory for $\begin{array}{l}CH_3-C-CO-NHC_6H_5\\ \qquad\ \,|\\ \qquad CH-COOH.\end{array}$	Found.
C	64.39	64.67
H	5.36	5.37

The compound forms large white rhombic prisms which melt at 175°. It is insoluble in cold water and dilute chlorhydric acid, but dissolves in dilute alkalies to form salts, and acids precipitate the unchanged substance from such solutions. It is soluble in hot alcohol, moderately in cold.

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[1] In view of the differences in the results obtained by Anschütz and Wirtz (Annalen **239**, 148), I repeated this experiment, unfortunately on a small scale, as I had but a few grams of maleic acid at my disposal. The compound separates as crystalline plates that are soluble in dilute chlorhydric acid, but after several crystallisations from alcohol become insoluble in it, in fact they are insoluble in the strong acid. It is evident that the compound undergoes some change during crystallisation, and I am surprised that Anschütz and Wirtz did not take the trouble to crystallise their product before making note of supposed differences, as it is evident that reference was made in our preliminary note to the crystallised product. In regard to the melting point, the specimen I examined decomposed partially before that temperature is reached, so that it is impossible to give a well-defined melting point. The substance dissolves in dilute alkalies, but strong alkaline solutions set aniline free. An analysis of the product gave the following figures :

0.2878 gram substance dried in a vacuum gave 0.6087 gram CO_2 and 0.150 gram H_2O.

	Theory for $C_{10}H_{11}NO_4$.	Found.
C	57.41	57.68
H	5.26	5.76

The product analysed by Mr. Palmer was probably dried in vacuo at 100°, when it lost a molecule of water, although, as no mention is made in his notes of the conditions of drying, this must remain a surmise on my part. Whether the compound is the acid anilide with a molecule of water of crystallisation, can only be settled by a more detailed examination.—A. M.

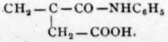
The substance, obtained by Gottlieb[1] by treating citraconanil with ammonia and precipitating the solution with acetic acid, may be identical with our compound, but, as there are two isomeric acid anilides of citraconic acid possible, the identity must be left to be decided by a more detailed account of Gottlieb's compound, who mentions that a small yield was obtained by his method, while by the method just described almost the theoretical yield can be obtained. Gottlieb describes his compound as small, glittering crystals. A solution of dianiline citraconate does not form an anilide on standing in the cold, but on boiling the anil separates. It melts at 98°.

Behavior of Itaconic Acid towards Aniline.

Anschütz and Petri[2] and also Markownikoff[3] have observed that itaconic acid or its silver salt, when treated with acetyl chloride, gives an anhydride of the acid. This reaction cannot be considered as a proof that itaconic acid belongs to the maleic acid series, as the method used also causes the formation of anhydrides with acids that certainly do not belong to it, as succinic and pyrotartaric acids. The following experiments on the behavior of itaconic acid towards aniline show quite conclusively, however, that it is to be classified as a member of the maleic series.

Five grams of itaconic acid were dissolved in 50 grams of water, and 3 grams of aniline added. This solution was heated to boiling for half an hour, in a flask connected with a condenser, and on cooling gave a copious precipitate, which was purified by crystallisation from dilute alcohol.

0.3664 gram substance gave 0.8657 gram CO_2 and 0.1804 gram H_2O.



	Theory for $CH_2-\underset{\displaystyle CH_2-COOH.}{C}-CO-NHC_6H_5$	Found.
C	64.39	64.45
H	5.36	5.44

It crystallises in plates that melt at 189°, and is identical with the product obtained by Gottlieb[4] by heating solid acid aniline itaconate. It is insoluble in dilute chlorhydric acid, but dissolves in dilute alkalies, and is precipitated unchanged from this solution by adding an acid.

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[1] Annalen der Chemie **77**, 280.

[2] Berichte der deutschen chemischen Gesellschaft **13**, 1538.

[3] *Ibid.* **13**, 1844.

[4] Annalen der Chemie **77**, 284.

The same compound is formed by allowing a solution of acid aniline itaconate in ten parts of water to stand for several days in the cold, when rhombic prisms that melt at 189° are deposited. It was impossible to obtain the anil of itaconic acid by heating an aqueous solution of its aniline salts.

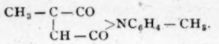
Behavior of Citraconic Acid towards some other Aromatic Primary Amines.

It seemed to be of interest to ascertain whether other primary aromatic amines than aniline would show similar reactions with citraconic acid, and to what degree the basic property of the amine could be decreased without its losing the power of giving the anilide reaction.

A solution of acid paratoluidine citraconate in five parts of water gives, on warming, a crystalline precipitate that melts at 161°, and when crystallised from absolute alcohol melted at 166°. This compound is probably the acid toluide. When it is crystallised several times from boiling water it is converted into a different substance, which is the tolil.

0.3670 gram substance gave 0.9625 gram CO_2 and 0.1885 gram H_2O.

0.3631 gram substance gave 0.9552 gram CO_2 and 0.1815 gram H_2O.

Theory for 

$\begin{matrix} CH_3-C-CO \\ | \\ CH-CO \end{matrix} > NC_6H_4-CH_3.$

	Theory	Found.	
C	71.64	71.50	71.71
H	5.46	5.69	5.56

Citracontolil crystallises from water in long silky needles that melt at 114.5°. It is insoluble in dilute chlorhydric acid and alkalies, soluble in alcohol and hot water, sparingly soluble in cold water.

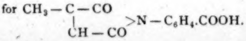
Mono-ortho-toluidine citraconate dissolves readily in cold water. This solution becomes turbid on boiling, and if the heating is continued for about half an hour an oil separates. On cooling, a further quantity of oil was deposited, that on standing gradually became solid. It was insoluble in dilute chlorhydric acid, and was evidently a toluidide.

a-Naphthylamine citraconate in aqueous solution gives an oily precipitate on boiling, which solidifies on standing. The compound crystallises from alcohol as yellow plates that melt at 141° and may be sublimed unchanged. The compound is insoluble in dilute chlorhydric acid and alkalies, and probably represents citracon-naphthylimide.

A solution of β-naphthylamine citraconate also deposits a substance on boiling. This compound, crystallised from water, forms yellow feathery needles that melt at 170° and may be sublimed without change. It is insoluble in dilute chlorhydric acid.

The behavior of metamido-benzoic acid towards citraconic acid is of particular interest, as this substance is so weak a base that it does not form salts with monobasic organic acids. A solution of one part of citraconic acid in five of water dissolves metamido-benzoic acid (equivalent proportions) very slowly in the cold, rapidly on warming. When this solution is boiled a crystalline precipitate is soon deposited, which was purified by crystallisation from hot water.

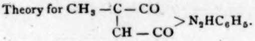
0.3802 gram substance gave 0.8710 gram CO_2 and 0.1366 gram H_2O.

	Theory for  $\left.\begin{array}{l}CH_3-C-CO\\ \quad\;|\\ \quad CH-CO\end{array}\right>N-C_6H_4.COOH.$	Found.
C	62.33	62.46
H	3.89	4.00

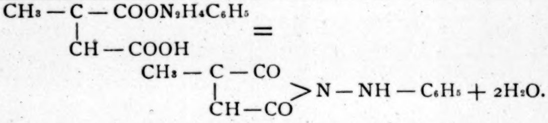
Meta-citraconanil-carboxylic acid crystallises from water as fine prismatic needles that melt at 218°. It is soluble in hot alcohol and water, sparingly soluble in cold water, and insoluble in dilute chlorhydric acid. Dilute solutions of alkalies dissolve it to form salts.

Although it did not seem likely that citraconic acid would form an anilide with sulphanilic acid, as this amido compound does not even form salts with mineral acids, an experiment was made that gave negative results. Corresponding to the anilides, derivatives of phenylhydrazine have been obtained by using analogous methods. Our expectation that phenylhydrazine would form an azide on heating with aqueous citraconic acid was fulfilled. A solution of monophenylhydrazine citraconate in ten parts of water, when boiled, turns yellow, and a crystalline precipitate soon separates, which is considerably increased as the solution cools. It was purified by crystallisation from alcohol.

0.3903 gram substance gave 0.9441 gram CO_2 and 0.1851 gram H_2O.

	Theory for  $CH_3-\begin{array}{l}C-CO\\ \vert\\ CH-CO\end{array}\!>N_2HC_6H_5.$	Found.
C	65.34	65.89
H	4.95	5.24

It crystallises in long, bright yellow prismatic needles that melt at 160°, and are sparingly soluble in cold, pretty soluble in hot water, and readily in hot alcohol. It is insoluble in dilute chlorhydric acid. As citraconic acid does not form anilides with secondary amines, the reaction is very likely correctly expressed by the following equation:



$$\begin{array}{l} CH_3-C-COON_2H_4C_6H_5 \\ \qquad\vert \\ \qquad CH-COOH \end{array} = \begin{array}{l} CH_3-C-CO \\ \qquad\vert \\ \qquad CH-CO \end{array}\!\!>N-NH-C_6H_5+2H_2O.$$

Behavior of the Phthalic Acids towards Aniline.

The phthalic acids are distinguished by the capability of the ortho acid of forming an anhydride. All attempts to obtain a similar derivative of the other two acids have been futile. As the ease that polybasic acids form anhydrides evidently is in close relationship with the anilide reaction, and ortho-phthalic acid forms its anhydride with readiness, it seemed of interest to examine whether this reaction would not serve to distinguish between these isomeric acids.

The acid aniline phthalate is difficultly soluble in cold, but dissolves readily in hot water. If a solution of this salt in six parts of water is boiled in a flask connected with a cooler, it will be noticed that a precipitate gradually separates from the hot solution, that increases as the solution cools. The acid aniline salt is readily decomposed by dilute chlorhydric acid, forming the chlorhydrate and free acid, while the precipitate formed by boiling a solution of the salt is insoluble in that acid. It melts at 203°, and agrees in all its properties with phthalanil. The anil is also formed by boiling an aqueous solution of the neutral aniline salt, and when a solution of the acid salt is allowed to stand at ordinary temperature for some days.

Isophthalic acid also forms an acid aniline salt, but its solution in water may be boiled for hours without anything separating from it, and on cooling yields unchanged salt that is readily soluble in dilute chlorhydric acid. An aqueous solution of the neutral aniline salt gave the same result.

Terephthalic acid unites with aniline, but with difficulty, and the salt is unstable in presence of considerable water. A solution in a small quantity of hot water was boiled for an hour without any change taking place, and a like result was obtained by heating an aqueous solution of the neutral salt.[1]

Behavior of some Saturated Polybasic Acids towards Aniline.

It seemed desirable to show that the property of forming anilides on heating an aqueous solution of aniline salts is characteristic of a certain group of unsaturated acids, and not shown by polybasic saturated fatty acids. We shall make but a brief mention of our experiments in this direction, and include in it several experiments with unsaturated acids. Acid aniline oxalate is difficultly soluble in hot water. After boiling its aqueous solution for a long time, long flat prisms separate on cooling. They are soluble in dilute chlorhydric acid, and consist of unchanged salt.

Acid aniline malonate dissolves readily in cold water. Its solution undergoes no change on boiling.

Acid aniline succinate is difficultly soluble in cold water, but dissolves in hot. It undergoes no change when its aqueous solution is boiled.

One part of tartaric acid in ten parts of water will dissolve sufficient aniline to form the acid salt. On boiling this solution a precipitate separates. This, however, represents an aniline tartrate, as it is immediately decomposed by dilute chlorhydric acid.

Acid aniline citrate is soluble in cold water, and does not change when its aqueous solution is boiled.

Acid aniline camphorate dissolves in boiling water, and after cooling separates unchanged as an oil that gradually solidifies.

Acid aniline pyrotartrate (obtained by reducing citraconic acid) is soluble in hot water, and undergoes no change when its aqueous solution is boiled.

Acid and neutral aniline mucates do not form anilides when their aqueous solutions are boiled.

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[1] There is no doubt but that a very convenient method for detecting the presence of carboxyls in ortho position in aromatic acids can be based on their forming anilides from aqueous solutions of their aniline salts. The existence of a second orthophthalic acid that would stand in the same relation to orthophthalic acid that fumaric does to maleic acid also seems probable.

Summary.

I. Unsaturated polybasic organic acids may be divided into two classes according as their aniline salts, in aqueous solution, split off water to form anilides or remain unchanged. The anilide-forming acids are classified as belonging to the maleic acid series, and the others to the fumaric acid series.

II. Of the acids as yet examined the following belong to the maleic series: maleic, brommaleic (m. pt. 128°), dibrommaleic acid (123°), citraconic, itaconic, bromcitraconic, aconitic and orthophthalic acids. To the fumaric series: fumaric, bromfumaric (178°), chlorfumaric (191°), mesaconic, mucic, camphoric, and iso- and terephthalic acids.

III. Chlor- and bromfumaric acids, in aqueous solution, when boiled with aniline are converted into the anil of phenyl-amidomaleic acid.

IV. The bromine atoms of dibrommaleic acid are symmetrically grouped.

V. The acids of the maleic series give the anilide reaction with all primary salt-forming aromatic amines, but not with secondary or tertiary aromatic bases. On this property a method of separating these bases has been based.

VI. The acetates of primary amido-benzenes are not decomposed by cold water, while those of the secondary or tertiary amines, if formed at all, are decomposed. A separation of basic mixtures has been based on these properties.

VII. Saturated polybasic acids do not give the anilide reaction.[1]

VIII. The results obtained in this investigation cannot be brought in harmony with the hypothesis that acids of the maleic series contain a divalent carbon.

IX. The anhydride and anilide formation of orthophthalic and similar acids probably depends on their belonging to the maleic series, and not on the positions of the carboxyls as represented by the constitutional formulas now in use.

X. Aqueous solutions of the citraconates of fatty amines do not form alkylamides.

TUFTS COLLEGE, MASS.

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[1] This rule is certainly not without exceptions, as experiments with the aniline salts of the dibenzyldicarboxylic acids have shown, which will be published later. The behavior of aniline salts of polybasic organic acids in their aqueous solution will be continued, and I wish to reserve the further examination of the reaction until my research is completed.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON THE ETHERS OF ORGANIC ACIDS, AND ON SOME DERIVATIVES OF ACETIC ACID.

BY ARTHUR MICHAEL.

Organic chemistry is indebted to A. Cahours[1] for the introduction of one of its most valuable reagents. The French chemist showed that phosphorus pentachloride acts on aromatic acids, forming the corresponding chlorides, and on aromatic aldehydes to form compounds in which the oxygen of the carbonyl is replaced by two chlorine. The great importance of the discovery was shown a few years later by Gerhardt,[2] in whose hands the chlorides were made the starting-point of those famous researches on organic anhydrides and amides. Gerhardt also obtained, by a modification of Cahours' reaction, the chlorides of fatty acids; and Würtz[3] and Geuther[4] showed that phosphorus pentachloride acts on ethyl aldehyde to form ethylidene chloride. Friedel[5] proved that the oxygen of acetone can be replaced by two chlorine by means of the reagent, and Schischkoff and Rösing[6] that benzoyl chloride can be converted into phenyl-chloroform by heating it with the pentachloride in a sealed tube, a reaction that Hübner[7] found to be also applicable to acetyl chloride. These reactions have been shown to be typical for the groups of organic substances they represent by other chemists, and it is now generally considered that, with a few exceptions of complicated products, substances containing hydroxyl may be converted by the chlorides of phosphorus into derivatives in which the hydroxyl is replaced by chlorine, and those containing carbonyl into derivatives in which the carbonyl oxygen is replaced by two chlorine.

There is, however, a noticeable exception to the latter rule in the behavior of organic ethers towards phosphorus pentachloride. Cahours in his paper remarks that phosphorus pentachloride does not react on benzoic ether. On the other hand, Geuther[8] obtained two chlorcrotonic acids by treating the product of the action of phosphorus pentachloride on acetylacetic ether with water, a result that indicates the formation of the chlorides of these acids; and Richter[1] obtained the chloride of monoethyl-oxalic acid by heating oxalic ether with the same reagent. In view of the stability of alkyloxyl in ethers, as was shown by Cahours, who obtained the chloride of anisic acid by the action of phosphorus pentachloride on the acid, and by Henry[2] on the fatty series, it seemed not unlikely that the alkyloxyl of the ethers of organic acids would show a certain, although relatively less, stability than these groups do in the ethers; and, bearing this in mind, the product obtained by Richter may be supposed to represent a secondary stage of the reaction, it being formed by the decomposition of a substance formed from oxalic ether by replacing an oxygen by two chlorine:

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[1] Ann. Ch. Phys. [3] **23**, 327.

[2] *Ibid.* [3] **37**, 285; Gerhardt and Chiozza, Comptes rend. **37**, 86.

[3] Ann. Ch. Phys. [3] **59**, 104.

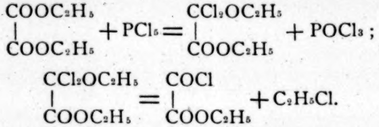
[4] Annalen der Chemie **105**, 321.

[5] Bull. Soc. Chim. 1859, 26.

[6] Compt. rend. **46**, 367.

[7] Annalen de Chemie **120**, 330.

[8] Zeitsch. für Chemie, 1871, 237.



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + PCl_5 = \begin{array}{l}CCl_2OC_2H_5\\ |\\ COOC_2H_5\end{array} + POCl_3;$$

$$\begin{array}{l}CCl_2OC_2H_5\\ |\\ COOC_2H_5\end{array} = \begin{array}{l}COCl\\ |\\ COOC_2H_5\end{array} + C_2H_5Cl.$$

It seemed of interest to ascertain whether this is the true conception of the reaction, and also to ascertain whether other ethers would not yield such intermediate products, when examined in view of their instability. If the reactions proceed in this manner, it is evident that the aromatic ethers of acids would show a greater stability than the corresponding alkyl derivatives; as, to take an example, it is obvious that the phenyl of the compound $R-CCl_2OC_6H_5$ would be much less likely to separate from the oxygen than the ethyl of $R-CCl_2-OC_2H_5$. My experiments began with phenyl acetate, as it seemed likely that the reaction would be less complicated with the ether of a monobasic acid than with the ether of a dibasic acid.[3]

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[1] Berichte der deutschen chemischen Gesellschaft **10**, 2228.

[2] *Ibid.* **2**, 276, 664, 710; **3**, 704.

[3] A preliminary note on this work was sent to the Berichte for publication on the 17th of March, 1886, and was published on the 10th of May. On the 28th of May Anschütz and Schönfeld sent in a short paper to the same journal (page 1444) in which they showed that one of the carbonyl oxygen of amyl and propyl oxalates may be replaced by means of phosphorus pentachloride by chlorine. Although I was pleased to have my views on the action the pentachloride on organic ethers confirmed, I must express my surprise that these chemists did not deem it an obligation towards me to send in their results, which they distinctly state were completed when my note appeared, immediately after the appearance of my note, instead of waiting longer than two weeks before doing it.

Action of Phosphorus Pentachloride on Phenyl Acetate.

Phosphorus pentachloride does not act on phenyl acetate in the cold, but readily at a moderate heat. A mixture of the substances, in molecular proportions, was brought into a flask connected with a cooler and heated at 100° for four hours. The evolution of chlorhydric acid began soon after heating, and was practically ended after heating two hours, although a very small quantity of the gas continued to be given off on longer heating. In one experiment the evolution of acid continued fifteen hours, but a larger yield of the product of the reaction is not obtained by continuing the operation. The homogeneous liquid was then distilled until a good part of the phosphorus oxychloride and trichloride that are formed in the reaction was driven off, and the residue poured into a considerable amount of cold water. After the violent reaction accompanying the conversion of the chlorides into acids was over, the heavy oily residue was separated from the supernatant liquid, and boiled for several hours, in a flask connected with an upright cooler, with a strong solution of caustic soda. This operation decomposed unchanged phenyl acetate and phenyl phosphate, which is also formed in the reaction. The alkaline mixture was then treated with steam as long as an oil passed over. If, however, cold water was used in the condenser, the substance often came over as a solid. The oil solidified on cooling to a mass of large white crystals, and the solid substance was purified by crystallising four times from a small amount of hot alcohol. The analyses gave the following results:

0.2635 gram substance dried in vacuum gave 0.4170 gram CO_2 and 0.0583 gram H_2O.

0.2712 gram substance dried in vacuum gave 0.5210 gram AgCl.

	Theory for $C_8OCl_3H_5$.	Found.
C	42.95	43 16
H	2.23	2.52
Cl	47.65	47.53

The substance crystallises from alcohol in large stellate groups of crystals, but if a relatively large proportion of alcohol is used, long white needles are deposited. It melts at 26.5° without decomposition. It is insoluble in cold and hot water, readily in hot, pretty soluble in cold alcohol, and also dissolves easily in hot chloroform, ligroin and benzene, but less in these solvents when cold. The substance passes over readily with steam, and, as its preparation indicates, it can be boiled with strong alkali without undergoing a change. It distills at a high temperature with partial decomposition, but unchanged in a vacuum, the boiling point being 120° under a pressure of 26 mm., and 106°–108° under a pressure of 12 mm. The formation of a substance having the composition $C_8OCl_3H_5$ from phenyl acetate and phosphorus pentachloride necessitates the assumption that the carbonyl oxygen is replaced by chlorine in the operation; but the hydrogen of the compound thus formed (it is also possible that the two reactions are simultaneous) is extremely susceptible to chlorination, although an excess of unchanged phenyl acetate is evidently present. To form a correct idea of the changes that take place in this remarkable reaction, the various stages that may be supposed to occur are represented by equations:

$$CH_3-COOC_6H_5+PCl_5=CH_3-CCl_2OC_6H_5+POCl_3;$$
$$CH_3-CCl_2OC_6H_5+2PCl_5=$$
$$CHCl_2-CCl_2OC_6H_5+2PCl_3+2HCl;$$
$$CHCl_2-CCl_2OC_6H_5=CCl_2-CClOC_6H_5+HCl.$$

The compound is therefore trichlor-phenoxyethylene or trichlor-vinyl-phenyl ether, and is analogous in its chemical nature to the substance obtained by Geuther[1] by the action of sodium ethyl oxide on perchlorethylene:

$$CCl_2-CCl_2+NaOC_2H_5=CCl_2-CClOC_2H_5+NaCl.$$

If this view of the constitution of the new substance be correct, it can be synthesised in an analogous manner; that is, by the action of perchlorethylene on sodium phenyl oxide. To realise this synthesis it is not necessary to prepare sodium phenyl oxide, as a solution of phenol in alcoholic sodium ethyl oxide acts as the first-named reagent, and in all probability contains it—in fact, that it gives the result described below may be accepted as a decisive proof:

$$C_2H_5ONa+C_6H_5OH=C_2H_5OH+NaOC_6H_5.$$

An absolute alcoholic solution of sodium, phenol and perchlorethylene, in equivalent proportions, was heated for eight hours in a sealed tube at 110°–115°.[2] The product of the reaction was thrown into water, the mixture extracted with ether, and the ethereal solution, after drying over calcium chloride, heated on a water-bath until the ether was expelled. The residue was distilled under a pressure of 10–12 mm., and passed over almost completely from 105°–107°, which is the boiling point of trichlor-phenoxyethylene. An analysis showed it to be that substance.

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[1] Jr. prkt. Chem. [2] **7**, 105.

[2] If sodium ethyl oxide and phenol are used in larger proportion and the tube heated to a higher temperature, different products seemed to be formed, which were not further examined.

0.2186 gram oil gave 0.4731 gram AgCl.

	Theory for $CCl_2CClOC_6H_5$.	Found.
Cl	47.65	47.31.

The formation of trichlor-phenoxyethylene from perchlorethylene conclusively proves the accepted constitution as correct, and the reaction may be represented as follows:

$$CCl_2 - CCl_2 + NaOC_6H_5 = CCl_2 - CClOC_6H_5 + NaCl.$$

It was assumed that the formation of trichlor-phenoxyethylene was preceded by that of a substance of the constitution $CCl_2H - CCl_2OC_6H_5$. Such a compound would, when treated with alkalies, decompose into chlorhydric acid and the final product of the reaction. It seemed of interest to ascertain whether the elimination of chlorhydric acid takes place in the reaction or during the treatment with alkalies, and with this object in view, a portion of the product of the action of phosphorus pentachloride on phenyl acetate was directly distilled in a vacuum. The portion passing over between 120°–130° under 25 mm. pressure was fractionated again under the same conditions, and passed over principally between 121°–125°, a temperature that corresponds to the boiling point of trichlor-phenoxyethylene. A portion of this oil,[1] which agreed in its properties with the trichlor compound, was analysed.

0.2439 gram oil gave 0.4546 gram AgCl.

	Theory.	Found.
Cl	47.53	46.12

The product obtained by direct distillation probably contained a small amount of a substance with a less percentage of chlorine, and having very nearly the same boiling point as trichlor-phenoxyethylene, but there can be no doubt that the substance analysed was largely composed of the compound. The formation of the substance in this manner shows that it is a direct product of the action of phosphorus pentachloride on phenyl acetate.[1]

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[1] Pure trichlor-phenoxyethylene, after a distillation in a vacuum, remains an oil at ordinary temperature. It would seem as if a slight decomposition takes place that lowers its melting point.

Action of Phosphorus Pentachloride on Metaphenylene Acetate.

It seemed of interest to ascertain whether the acetyl derivatives of polyatomic phenols would behave towards the pentachloride in a manner similar to the phenol derivative.

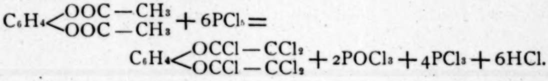
A mixture of metaphenylene acetate and pentachloride, in the proportion of one molecule of the first to two molecules of the second compound, was heated in a water-bath as long as chlorhydric acid was given off. The product of the reaction was thrown into water, the residue heated with strong alkali, and finally treated with steam. An oily substance passed over that soon solidified. This was crystallised four times from alcohol, and analysed with the following results:

0.2770 gram substance dried in a vacuum gave 0.6453 gram AgCl.

0.2128 gram substance dried in a vacuum gave 0.4495 gram AgCl.

	Theory for $C_6H_4<\begin{smallmatrix}OCCl-CCl_2\\OCCl-CCl_2\end{smallmatrix}$.	Found. I.	Found. II.
Cl	57.72	57.61	57.53

The formation of the substance, meta-trichlorvinyl-phenylene ether, may be represented as follows:



$$C_6H_4<\begin{matrix}OOC-CH_3\\OOC-CH_3\end{matrix}+6PCl_5=$$
$$C_6H_4<\begin{matrix}OCCl-CCl_2\\OCCl-CCl_2\end{matrix}+2POCl_3+4PCl_3+6HCl.$$

It crystallises from alcohol in long prisms with domes that melt at 53°-54°. It is insoluble in hot water, readily soluble in hot, pretty soluble in cold alcohol. From a warm alcoholic solution it separates on cooling as an oil that often remains liquid until touched with a solid substance. The substance is quite soluble in cold benzene, ligroin, chloroform, and ether.

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[1] It might be supposed that a larger proportion of pentachloride to phenyl acetate would greatly increase the yield of trichlor-phenoxyethylene. Experiments using two and three molecules of chloride to one of acetate showed, however, that the amount thus obtained was not very much greater than when but one molecule of chloride is used. In fact, considering the ease with which phenyl acetate may be made, it would seem more advantageous to use molecule for molecule than to use the chloride in larger proportion.

Action of Phosphorus Pentachloride on Paraphenylene Acetate.

The reagents, two molecules of chloride to one of acetate, were treated as in the corresponding experiment with the meta-acetate. Instead, however, of heating with alkali, the crude product of the reaction was directly treated with steam, when long white needles passed over. These were purified by several crystallisations from alcohol, and analysed.

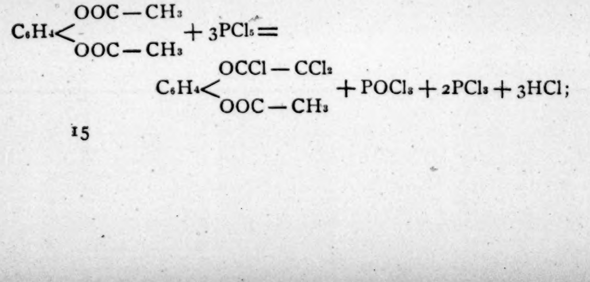
0.2447 gram substance dried in a vacuum gave 0.3570 gram CO_2 and 0.0550 gram H_2O.

0.2464 gram substance gave 0.450 gram AgCl.

	Theory for $C_8Cl_3H_5O_2$.	Found.
C	40.01	39.78
H	2.09	2.48
Cl	44.47	45.12

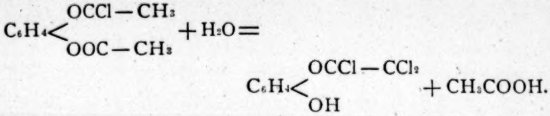
The substance crystallises in long white fibrous needles that very closely resemble asbestos in form and appearance. It is slightly soluble in hot water, from which it separates as needles on cooling. In ether, chloroform, and benzene it dissolves readily in the cold, in hot alcohol very soluble, it is also quite soluble in cold. From a saturated hot alcoholic solution it separates in plates. It also dissolves readily in hot ligroin, but only moderately in the cold solvent. Warmed with caustic alkalies it goes into solution and does not separate from the solution on cooling, but the addition of an acid causes a precipitate of the original substance. In acetyl chloride it dissolves with the evolution of chlorhydric acid and formation of an acetyl derivative. It melts without decomposition at 66°–66.5°, but decomposed completely in an attempt at distillation.

The properties of this substance show that it contains a free hydroxyl; in fact, but one of the acetyl groups of the mother substance has undergone the change characteristic for the reaction, and the second unchanged group has been removed by the action of water, probably on treating the crude product with steam.



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{OOC-CH_3}\\ \mathrm{OOC-CH_3}\end{matrix}+\mathrm{3PCl_5}=$$

$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{OCCl-CCl_2}\\ \mathrm{OOC-CH_3}\end{matrix}+\mathrm{POCl_3}+\mathrm{2PCl_3}+\mathrm{3HCl};$$



$$C_6H_4<\begin{matrix}OCCl-CH_3\\OOC-CH_3\end{matrix}+H_2O=C_6H_4<\begin{matrix}OCCl-CCl_2\\OH\end{matrix}+CH_3COOH.$$

It may be called paroxy-trichlor-phenoxyethylene.[1]

Action of Phosphorus Pentachloride on Phenyl Propionate.

In order to show that the reaction is general for aromatic ethers of other acids, a few preliminary experiments were made on the action of phosphorus pentachloride on phenyl propionate.

Twenty grams of the ether and fifty-eight grams of pentachloride were heated in a water-bath for twelve hours, the product thrown into water, and the oily residue heated with dilute alkali. On treating with steam, an oil passed over that could not be brought into a solid state. It was fractionated under 25 mm. pressure, when most of it passed over between 110° and 135°. By repeated fractionation it was separated into two portions, one boiling 115°-117° under 25 mm. pressure, and the other from 125°-130°. The chlorine estimations of the oil boiling at 115° gave results that agree with the constitution $C_9H_8OCl_2$.

0.2971 gram substance gave 0.3837 gram AgCl.
0.2613 " " " 0.3402 " AgCl.

	Theory for $C_9H_8OCl_2$.	Found.	
Cl	32.41	31.95	32.15

The oil resembles trichlor-phenoxyethylene in its properties, but would not solidify even at 0°. It is insoluble in water, but readily soluble in alcohol. Its constitution is probably $CH_3-CCl-CClOC_6H_5$:

$$CH_3-CH_2-COOC_6H_5+2PCl_5=CH_3-CCl-CClOC_6H_5+POCl_3+PCl_3+2HCl.$$

The fraction boiling between 125°-130° was very likely not a pure substance.

0.2543 gram oil gave 0.3967 gram AgCl.

	Theory for $CH_2Cl-CCl-CClOC_6H_5$.	Found.
Cl	42.01	38.57

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[1] In a preliminary notice on this reaction (Berichte **19**, 846), I gave this compound the isomeric constitution $C_6H_4\overset{O}{\underset{O}{>}}CCl-CHCl_2$. At the time of its publication I was unaware that the substance dissolves unchanged in alkalies and also forms an acetyl derivative—properties that exclude such a constitution.

Action of Phosphorus Pentachloride on Ethyl Benzoate.

Cahours in his memoir describes an experiment consisting of distilling the pentachloride with benzoic ether, which he found to pass over unchanged. This result was probably obtained by rapid distillation, when a part of the ether may escape without being acted on. The ether dissolves the chloride when heated to 100°, but even at that temperature a reaction takes place, although very slowly, as after two days' heating most of the chloride separated out of the solution on cooling. If the solution is heated to 110° the reaction also proceeds slowly, so that several days are necessary before a few grams of the pentachloride are completely converted into the oxychloride. At 140° in a sealed tube a much shorter time is needed; heating for about eight hours in a sealed tube sufficed to convert ten grams of pentachloride into oxychloride. The same products of the reaction were obtained in both cases. When the experiment was made in a sealed tube, the tube opened under pressure, and an inflammable gas was given off that contained chlorine and evidently consisted of ethyl chloride. The greater part of this compound remained in solution, and was given off when the liquid was heated to 40° or 50°. The contents of the tube were subjected to fractionation in a vacuum (12 mm.) and were easily separated into two fractions. The lower-boiling portion consisted of phosphorus oxychloride and the higher of benzoyl chloride, of which almost the amount indicated by theory was obtained. The action of the pentachloride on benzoic ether may be represented as follows:

$$C_6H_5COOC_2H_5 + PCl_5 = C_6H_5COCl + C_2H_5Cl + POCl_3.$$

Action of Phosphorus Pentachloride on Acetic Ether.

The ether and chloride, the first compound in excess, were heated in a sealed tube to 150°. On opening the tube ethyl chloride escaped, and by repeated fractionation of the liquid, unchanged ether, acetyl chloride, and phosphorus oxychloride were obtained.

An experiment with ethyl trichlor-acetate and pentachloride, heated in an oil-bath to 150°, showed that in this instance an analogous reaction took place. Trichlor-acetyl chloride, phosphorus oxychloride, and ethyl chloride were formed.

Remarks on the Preceding Experiments.

The results just described, although in no instance was a compound formed from an organic ether by replacing the carbonyl oxygen by chlorine, prove the point in question with the same degree of precision as if such a product had been isolated. The formation of trichlor-phenoxyethylene, and analogous substances, can be explained only by supposing that the carbonyl oxygen of the aromatic ethers was replaced by chlorine, forming derivatives of the general constitution $R-CCl_2OR$; but owing to the remarkable facility with which the pentachloride acts on this compound as an agent for chlorination, these derivatives could not be isolated.[1] These results leave but little doubt that the pentachloride also acts on alkyl ethers to form similar derivatives, but the point of decomposition of these products seems to be so near that of chemical action that it is likely that only in a few instances it will be found possible to isolate the intermediate products.

Not alone is this indicated by the results described in this paper, but our knowledge of the ease with which the carbonyl oxygen of the different members of the COOR group enters into reactions points to the same conclusion. From this point of view it is necessary to consider the formation of the chloride as the second phase of the action of phosphorus pentachloride on an organic ether:

$$R-COOR+PCl_5=R-CCl_2OR+POCl_3;$$
$$R-CCl_2OR=R-COCl+RCl.$$

It may be of interest to call attention to the fact that the formation of an acid chloride from an acid and pentachloride is also open to the same interpretation; at least it has become imperative that more conclusive experiments be made before the present view can be considered as proved:

$$R-COOH+PCl_5=R-CCl_2OH+POCl_3;$$
$$R-CCl_2OH=R-COCl+HCl.$$

The formation of chlorides by the action of dehydrating agents and chlorhydric acid on organic acids may be considered to consist of an addition and subsequent dehydration:[1]

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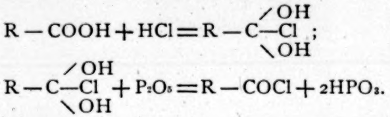
[1] I have made some experiments with phenyl benzoate and phenyl acetate, at a lower temperature than that described in the experiments described, that indicate the formation of this class of compounds, but owing to work of greater importance I have not found time to continue them. I hope to continue the investigation at some future time.



$$R-COOH+HCl=R-C\begin{matrix}\diagup OH\\ -Cl\\ \diagdown OH\end{matrix};$$

$$R-C\begin{matrix}\diagup OH\\ -Cl\\ \diagdown OH\end{matrix}+P_2O_5=R-COCl+2HPO_3.$$

Action of Phosphorus Pentachloride on Acetyl Chloride.

The ease with which phosphorus pentachloride replaces the hydrogen of the methyl in phenyl acetate suggested similar experiments with derivatives of acetic acid. Hübner[2] had already examined the action of the pentachloride on acetyl chloride, but in a sealed tube and at a high temperature. He obtained trichloracetyl chloride, ethenyl chloride, and pentachlor-ethane as products of the reaction.

Forty grams of acetyl chloride and two hundred grams of phosphorus pentachloride were heated in a flask connected with an inverted cooler for several weeks. The action proceeded slowly, and a considerable amount of pentachloride remained unchanged. The product was thrown into water, extracted with ether, and the extract, after drying, subjected to a fractional distillation. By repeating the operation a number of times, it was found possible to separate a portion boiling at 185°–187° that turned solid on cooling and melted at 62°–63°, and consisted of monochloracetic acid. A second fraction boiled between 193°–195°, and on cooling gave crystals melting at 52°. This compound was trichlor-acetic acid. Between these fractions a liquid was obtained that, although it could not be obtained pure, undoubtedly consisted largely of dichlor-acetic acid.

Action of Phosphorus Pentachloride on Monochloracetic Acid.

This reaction takes place much more readily than in the preceding instance. Ten grams acid and eighty-eight grams pentachloride (one molecule acid to four molecules chloride) were heated in a flask, and after twenty hours the chloride was entirely decomposed. The product was thrown into water, when a neutral oil remained, which was shaken out with a solution of sodium carbonate, dried, and fractionated a number of times. In this way an oil boiling from 120°–122° was isolated, which agrees in its properties with perchlorethylene.

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[1] L. Henry (Berichte **10**, 2043) suggested a somewhat similar explanation for the formation of organic ethers by the action of chlorhydric acid on a mixture of acid and alcohol.

[2] Annalen der Chemie **120**, 330; also Samosasky, Zeits. Chem. 1870, 105; and Frederici, Berichte der deutschen chemischen Gesellschaft **11**, 1971.

0.1836 gram oil gave 0.6339 gram AgCl.

	Theory for C_2Cl_4.	Found.
Cl	85.24	85.39

Besides perchlorethylene, higher-boiling products are formed, probably consisting of tetra- and pentachlorethene. On extracting the aqueous solution, obtained by pouring the product of the reaction into water, with ether, and fractionating, trichloracetic acid was separated :

$$CClH_2-COOH+3PCl_5= CCl_2-CCl_2+2POCl_3+PCl_3+3HCl.$$

Action of Phosphorus Pentachloride on Phenoxyacetic Acid.

Fifteen grams of acid and sixty grams of pentachloride were mixed in a flask connected with a cooler. A reaction takes place immediately, which is probably due to the formation of the chloride of the acid. The flask was then heated in a water-bath as long as chlorhydric acid came off, an operation that took about fifteen hours. On cooling, about one quarter of the amount of chloride taken separated. The product was thrown into water and filtered from the solid and oily substances that separated. This was treated with steam, when the oil passed over, and was found to consist of trichlor-phenoxyethylene. The residue remaining in the flask was crystallised four times from hot water.

0.2214 gram substance gave 0.1761 gram AgCl.
0.2485 " " " 0.1954 " "

	Theory for $CH_2OC_6H_4Cl-COOH$.	Found.	
Cl	19.04	19.60	19.46

The substance consists of rhombic prisms with domes that melt at 151°–152° without decomposition. It is moderately soluble in hot, sparingly in cold water. In alkalies it is soluble, and is precipitated out of the solution by addition of an acid. The substance has either the constitution $CH_2OC_6H_4ClCOOH$ or $CHClOC_6H_5COOH$, but the first constitution is probably correct, as its alkaline solution may be boiled without eliminating chlorine. It is therefore monochlor-phenoxyacetic acid:

$$C_6H_5O - CH_2 - COOH + 3PCl_5 =$$
$$C_6H_5O - CCl - CCl_2 + 2POCl_3 + PCl_5 + 3HCl;$$
$$C_6H_5O - CH_2 - COOH + 2PCl_5 =$$
$$C_6H_4ClOCH_2 - COCl + POCl_3 + PCl_3 + 2HCl.$$

Tufts College, Mass.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON ACETANILIDE.

By Arthur Michael.

The investigations of Gerhardt[1] and Wallach[2] on the action of phosphorus pentachloride on anilides and alkyl amides have shown that the oxygen of the carbonyl is replaced by chlorine, but that these compounds are not very stable, and decompose into compounds having the general constitution $R - CClNR$ and chlorhydric acid. Wallach, to whom we are principally indebted for the investigation of these interesting reactions, found that even the secondary products of the reaction are not stable in the heat, but pass over into basic substances free of chlorine. The investigation of the action of phosphorus pentachloride on the aromatic ethers of acetic acid led me to believe that an analogous reaction might be realised by the action of the pentachloride on anilides, and I made a few experiments with acetanilide in that direction, which, although they have not resulted in the synthesis of the anticipated class of substances, are not without interest. Forty-eight grams of pentachloride (3 mols.) were brought into a flask connected with a condenser, cooled with ice, and ten grams of powdered acetanilide (1 mol.) added. After the reaction, that takes place in the cold, when, as Wallach has shown, the compound $CH_3 - CClNC_6H_5$ is formed, the flask was allowed to stand at the ordinary temperature as long as chlorhydric acid came off, and the reaction was then completed by heating on a water-bath. The homogeneous mass—all the pentachloride was used up—was poured into water, when an oily mass remained undissolved that soon solidified. This substance was purified by crystallising from alcohol, and gave the following figures on analysis:

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[1] Ann. Ch. et Phys. [3] **53**, 302.

[2] Annalen der Chemie **184**, 1; **214**, 193, 257.

0.2458 gram substance gave 0.4258 gram CO_2 and 0.0804 gram H_2O.

0.2490 gram substance gave 0.3525 gram AgCl.

0.2734 gram substance gave 0.3827 gram AgCl.

	Theory for $C_8H_8Cl_2N_2$.	Found.		
C	47.29	47.24		
H	3.94	4.21		
Cl	34.97	...	34.94	34.64

The substance crystallises from alcohol in large white monoclinic prisms that melt undecomposed at 116.5°–117°. It sublimes slowly at 100°, forming small prisms with truncated end-faces. In water, cold and hot, it is insoluble, very soluble in warm, fairly in cold alcohol.

The substance has neutral properties, it being insoluble in acids as well as alkalies.

The action of pentachloride on acetanilide gives an entirely different result if, instead of heating on a water-bath, the mixture is allowed to remain in a moderately warm place for a long time. The mixture of pentachloride and anilide, in the same proportions as in the preceding experiment, was first cooled off on ice, and then allowed to stand at a temperature of about 35° for a week, when the greater part of the pentachloride was decomposed. It was noticed that after a number of days a yellow crystalline substance began to separate from the clear supernatant liquid. The contents of the flask were poured into water, and the insoluble residue purified by four crystallisations from alcohol.

I. 0.2621 gram substance gave 0.5522 gram CO_2 and 0.107 gram H_2O.

II. 0.2482 gram substance gave 0.5251 gram CO_2 and 0.1029 gram H_2O.

III. 0.2534 gram substance gave 0.3172 gram AgCl.

IV. 0.2015 gram substance gave 0.2529 gram AgCl.

	Theory for $C_{38}H_{36}Cl_7N_4$.	Found.			
		I.	II.	III.	IV.
C	57.32	57.47	57.54		
H	4.56	4.54	4.60		
Cl	31.00	...	...	30.96	31.03

The compound forms concentric groups of long lemon-colored needles that melt at 227°–229°, but begin to darken at 210°. It is insoluble in hot water, benzene and ether, moderately soluble in hot chloroform, readily in glacial acetic acid and hot alcohol, pretty soluble in cold alcohol. Like the preceding compound it is insoluble in acids and alkalies.

It would be useless to speculate on the constitution of these substances until a more detailed investigation of their behavior towards reagents has been made. The research will be continued in this direction, and it is also proposed to examine other anilides, as well as alkyl amides, in a similar manner.

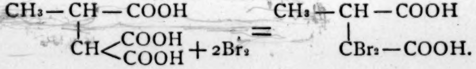
TUFTS COLLEGE, MASS.

PRELIMINARY NOTES.

BY ARTHUR MICHAEL.

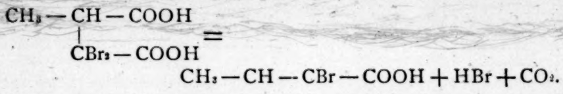
The approaching close of laboratory work for the present college year finds myself and co-workers with a number of unfinished investigations. It was thought advisable to state briefly the principal results that we have obtained, before the publication of the papers in full.

I. About five years ago Bischoff and Emmert[1] examined the action of bromine on propenyl-tricarboxylic acid, and obtained, besides other compounds, a dibrompyrotartaric acid that is isomeric with the three acids obtained by addition of bromine to ita-, citra- and mesaconic acids. The discoverers do not attempt to give a constitutional formula to this interesting acid; but, keeping the behavior of malonic acid and its derivatives towards bromine in mind, there can be no doubt that the reaction is represented by the following equation:



$$\begin{array}{l} CH_3-CH-COOH \\ \qquad | \\ \qquad CH<^{COOH}_{COOH} + 2Br_2 \end{array} = \begin{array}{l} CH_3-CH-COOH \\ \qquad | \\ \qquad CBr_2-COOH. \end{array}$$

This interpretation is corroborated by the fact that α-bromcrotonic acid was found among the products of the reaction:[2]



$$\begin{array}{l} CH_3-CH-COOH \\ \qquad | \\ \qquad CBr_2-COOH \end{array} = \\ CH_3-CH-CBr-COOH + HBr + CO_2.$$

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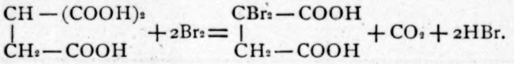
[1] Berichte **15**, 1107.

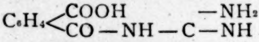
[2] *Ibid.* **14**, 616.

This explanation of the reaction made it very probable that the third possible dibromsuccinic acid would be obtained by the action of bromine on ethenyl-tricarboxylic acid:



$$\begin{matrix} CH-(COOH)_2 \\ | \\ CH_2-COOH \end{matrix} + 2Br_2 = \begin{matrix} CBr_2-COOH \\ | \\ CH_2-COOH \end{matrix} + CO_2 + 2HBr.$$

I have made a number of experiments by heating bromine and the acid in a sealed tube at 100°, and have obtained a dibromsuccinic acid which in its properties very closely resembles the symmetrical dibromsuccinic acid obtained by addition of bromine to maleic acid. However, it is extremely probable that the unsymmetrical acid would pass over into the symmetrical compound when exposed to the conditions of the experiment, and I shall repeat the experiments except that the substances will be allowed to act in the cold, which were the conditions that gave the unsymmetrical dibrompyrotartaric acid.

II. It is customary in examining the reactions of guanidine to use the carbonate, but I have found that an alcoholic solution of guanidine sulphocyanate and sodium ethylate acts as free guanidine, and gives the reactions in a much more satisfactory manner. Thus, by treating this solution in the cold with phenyl-mustard oil or benzile, the compounds described by Bamberger[1] and Wense[2] are obtained in almost theoretical yield. The solution gives reactions that cannot be realised with the carbonate. As an instance, it unites with phthalic anhydride to form the compound  $C_6H_4\!<\!\begin{matrix} COOH & & -NH_2 \\ CO-NH-C-NH \end{matrix}$ which crystallises in large prisms and melts at 202°. Of greater interest is the action of cyanogen on the solution. Two compounds are formed in the reaction, one crystallising in long needles, and the other in indistinct yellow crystals that are somewhat soluble in water, giving the solution a beautiful fluorescence that is very nearly like that caused by resocyanine. The formula of this substance is $(C_1N_1O_1H_2)_x$, but it is evidently of very complicated composition.[3]

III. With Mr. G. M. Browne, the reactions of guanidine have been further studied. Benzoic ether and an alcoholic solution of guanidine sulphocyanate with sodium ethylate (1 mol. salt to two mols. $NaOC_2H_5$) gives no less than four distinct crystalline products. The reaction is very complicated and its study not yet completed. Guanidine sulphocyanate, sodium ethylate, and malonic ether give a substance crystallising in plates with both acid and basic properties. It has the constitution $NH=C<\genfrac{}{}{0pt}{}{NH-CO}{NH-CO}>CH_2+H_2O$. A. Pinner[1] obtained a condensation product by the action of acetacetic ether on benzenyl-amidine, but was unsuccessful in a similar experiment with malonic ether. Such a product is obtained if an alcoholic solution of sodium malonic ether is used, and the reaction gives results with other bibasic ethers, as oxalic ether, sodium ethyloxide, and the amidine also give a condensation product.

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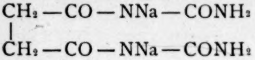
[1] Berichte der deutschen chemischen Gesellschaft **13**, 1580. [2] *Ibid.* **19**, 761.

[3] While working with cyanogen it occurred to me to see whether it would react on alcoholic solutions of sodium acetacetic and sodium malonic ethers, as these substances behave like bases towards many reagents. (This Journal **9**, 124.) I found that a reaction takes place with great readiness, forming crystalline salts. It is my intention to have the reaction further examined.

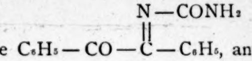
IV. We have also continued our investigation on the isomerism of unsaturated acids. On treating solid crotonic acid, dissolved in carbon bisulphide, with chlorine at a low temperature, $\alpha\beta$-dichlorbutyric acid was obtained. This acid crystallises in prisms that melt at 63°. By treating the acid with alcoholic soda a fourth chlorcrotonic acid is formed, which crystallises in needles and melts at 67°. The acid differs in its properties and in its salts from the three previously known chlorcrotonic acids ; and, as is evident from our previous work,[2] has the constitution $CH_3-CH-CCl-COOH$. It is the alpha-derivative of allocrotonic (isocrotonic) acid. We also made the observation that $\alpha\beta$-dichlorbutyric ether gives α-chlorcrotonic acid (97°) when treated with alkalies, which, in view of the fact that the free acid gives the allo-alphachlorcrotonic acid, is an interesting result.

V. With E. A. de Schweinitz, the action of sodium ethylate on mixtures of amides and ethers was continued. We find that urea, carbonic ether, and sodium ethylate give allophanic ether. From succinic ether, instead of carbonic, the compound



$$\begin{array}{l} CH_2-CO-NNa-CONH_2\\ |\\ CH_2-CO-NNa-CONH_2\end{array}$$

was obtained. Urea sodium ethylate and benzile give



$$C_6H_5-CO-\overset{\overset{N-CONH_2}{||}}{C}-C_6H_5,$$

and from acetamide with oxalic ether acetyloxamic acid was obtained. Organic ethers do not react on compounds as weakly basic as metanitraniline, but a reaction takes place if sodium ethyloxide is present; with oxalic ether the compound

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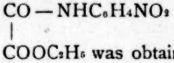
[1] Berichte der deutschen chemischen Gesellschaft **18**, 763.

[2] Berichte der deutschen chemischen Gesellschaft **19**, 1378, 1386; **20**, 550; Jr. prkt. Chemie [2] **35**, 257.



$$\begin{array}{l} CO-NHC_6H_4NO_2 \\ | \\ COOC_2H_5 \end{array}$$

was obtained.

Tufts College, Mass.

A METHOD FOR THE DETERMINATION OF BUTTER IN MILK.

By H. N. Morse and W. M. Burton.

[Second Communication.]

The method for the determination of butter in milk which was described in the preceding number of this Journal,[1] has been subjected to further examination in order to test its accuracy and to ascertain wherein its details could be improved.

The results obtained by a careful comparison indicate that it is quite as accurate as the gravimetric method; while the time required for its execution has been materially shortened by the discovery of the facts:

1st. That a much smaller number of washings with benzine than was formerly prescribed, suffices for the complete extraction of the butter.

2d. That the evaporation of the benzine before saponification is wholly unnecessary.

It has been found advantageous to change in some particulars the mode of procedure in making the determination.

We now begin the grinding of the copper sulphate and milk mixture while the mass is still somewhat moist, since by so doing the labor of reducing it to a fine powder is considerably diminished. Again, when the pulverised material is transferred to the tube for extraction, it is made more compact than formerly by tamping it down from time to time with a glass rod.

The extraction of the butter is effected in the following manner: Fifteen cubic centimeters of benzine are poured over the material in the extraction tube and drawn down with the aid of the filter pump until the whole of the mass to be extracted has become wet with the liquid, when the connection with the pump is closed.

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[1] 9, 108.

After about five minutes another portion of fifteen cubic centimeters of benzine is poured into the tube, and the whole of the liquid slowly drawn through with the aid of the pump into the flask.

As will be shown hereafter, this one extraction suffices in the majority of cases for the complete removal of the butter; nevertheless, for the sake of greater certainty, we are accustomed to wash with three other portions of benzine of 15 cubic centimeters each. The first two or three portions of the benzine are, of course, also used to wash the mortar.

In order to determine the butter thus extracted, the benzine solution, without previous evaporation, is treated with the requisite amount of alkali, and heated for twenty minutes upon the water bath, when the excess of the alkali is determined by means of the standard solution of hydrochloric acid. We have adopted the plan, which, for evident reasons, seems to be the safest, of standardising our solutions by means of the butter extracted by absolute ether from the dried residue of milk.

To prepare them, a solution of potassium hydroxide in 95 per cent. alcohol, slightly stronger than half normal, and a solution of hydrochloric acid containing a little more than 15 milligrams of acid to the cubic centimeter, are made, and the relation of the two to each other carefully determined. The known weight of butter, which has been obtained from the dried residue of 10 cubic centimeters of milk by extracting with absolute ether, evaporating, and drying at 100° to constant weight, is treated with the quantity of the alkaline solution which is equivalent to 25 cubic centimeters of the acid. The flask is then heated for twenty minutes upon the water-bath to the boiling point of the solution. Finally, the excess of the alkali is determined by means of the hydrochloric acid, with use of phenolphthalein as the indicator.

The difference between 25 cubic centimeters of the acid, to which the alkali added to the butter was equivalent, and the number of cubic centimeters of the acid which it is found necessary to use in neutralising the excess of the alkali, is the volume of the acid which is required to neutralise the alkali used up in the saponification of the known weight of butter. The acid is now so diluted that one cubic centimeter of it will neutralise the alkali required for the saponification of 100 milligrams of butter. The alkali is not diluted; but, in subsequent work, that quantity of it which is equivalent to 25 cubic centimeters of the standard acid is employed in every saponification. The difference, then, between twenty-five and the number of cubic centimeters of the acid required to neutralise the excess of the alkali, expresses in decimal parts of a gram the weight of the butter found.

Solutions of acid and alkali having one-half the strength of those already described, as will be shown hereafter, can also be employed.

Our experimental work embraces the following points, which will be taken up in the order of their statement:

I. A determination of the rapidity with which the butter is extracted by the benzine.

II. An examination of the question, whether it is necessary to evaporate the benzine before saponification.

III. A comparison of the gravimetric and saponification methods of estimating butter which has been extracted from the dried residue of milk by absolute ether.

IV. A comparison of the new with the gravimetric method.

V. An examination to determine whether more dilute standard solutions than those described give equally satisfactory results.

VI. A determination of the strength of the specimen of acid which had been standardised by butter and employed throughout the work.

VII. An examination to determine whether it is as well to dry the milk by means of anhydrous copper sulphate, as by evaporation, when it is desired to estimate the butter gravimetrically by the extraction method.

I.

To determine the rapidity with which the butter is extracted by benzine when the milk is dried by means of anhydrous copper sulphate, the material in the tube was treated with 15 cubic centimeters. This was then drawn down with the aid of the pump until the liquid had reached the bottom of the tube, when the connection with the pump was closed. After about five minutes, another equal portion of benzine was added and the whole drawn through into the flask. Afterwards, four other portions of benzine of 15 cubic centimeters each were drawn through the material to be extracted, each being, like the first, collected in a separate flask. These solutions, the first consisting of 30 cubic centimeters, the others of 15 each, are designated as 1st, 2d, 3d, 4th, and 5th extracts. Each was treated with alkali and saponified in the manner which has already been described.

In order to ascertain at the same time whether there is any marked difference, as regards efficiency, between very low boiling benzine and that collected at somewhat higher temperatures, two pairs of determinations were, in each case, made; one with benzine collected between 30° and 45°, and the other between 45° and 60°. The three specimens of milk which were employed are designated by the letters A, B, and C.

The lower boiling benzine was employed in making the determinations 1 and 2 of each series; while 3 and 4 were made with the benzine boiling between 45° and 60°.

A.

1.

1st extract gave 3.61 per cent. of butter.
2d–5th extracts gave 0.00 " "

2.

1st extract gave 3.61 per cent. of butter.
2d–5th extracts gave 0.00 " "

3.

1st extract gave 3.57 per cent. of butter.
2d " " 0.02 " "
3d–5th extracts gave 0.00 " "

4.

1st extract gave 3.64 per cent. of butter.
2d–5th extracts gave 0.00 " "

Results of the First Series.

1. 3.61 per cent. of butter.
2. 3.61 " "
3. 3.59 " "
4. 3.64 " "

B.

1.

1st extract gave 3.82 per cent. of butter.
2d–5th extracts gave 0.00 " "

2.

1st extract gave 3.74 per cent. of butter.
2d " " 0.09 " "
3d–5th extracts gave 0.00 " "

3.

1st extract gave 3.72 per cent. of butter.
2d " " 0.09 " "
3d–5th extracts gave 0.00 " "

4.

1st extract gave 3.84 per cent. of butter.
2d–5th extracts gave 0.00 " "

Results of the Second Series.

1. 3.82 per cent. of butter.
2. 3.83 " "
3. 3.81 " "
4. 3.84 " "

C.

1.

1st extract gave 4.36 per cent. of butter.
2d–5th extracts gave 0.00 " "

2.

1st extract gave 4.36 per cent. of butter.
2d–5th extracts gave 0.00 " "

3.

1st extract gave 4.27 per cent. of butter.
2d " " 0.07 " "
3d–5th extracts gave 0.00 " "

4.

1st extract gave 4.19 per cent. of butter.
2d " " 0.09 " "
3d " " 0.05 " "
4th–5th extracts gave 0.00 " "

Results of the Third Series.

1. 4·36 per cent. of butter.
2. 4·36 " "
3. 4·34 " "
4. 4·33 " "

The results obtained indicate that five extractions by the method described are more than sufficient to extract all of the butter, and that benzine boiling between 45° and 60° is nearly, if not quite, as efficient as that collected at lower temperatures. We have made no experiments with benzine collected at temperatures above 60°.

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II.

In order to determine whether it is necessary to evaporate the benzine before adding the alkali for the purpose of saponifying the butter, six parallel determinations were made. The benzine in two cases was completely evaporated; in two others it was reduced to one-half of its original volume; while in the case of the third pair the alkali was added to the solution of butter without previous evaporation. The results were:

I.	II.
3·53 per cent. of butter.	3·54 per cent. of butter.
3·52 " "	3·53 " "

III.

3·54 per cent. of butter.
3·52 " "

The presence of the benzine does not appear to retard the saponification of the butter; and the little which remains in the flask after heating for 20 minutes upon the water-bath does not obscure the end-reaction when the excess of the alkali is determined by means of the standard acid.

III.

To test the agreement between the results obtained by the gravimetric method and those obtained by saponification with the use of solutions which had been standardised by the butter extracted from milk, we have made, in all, twenty-two parallel determinations, employing for the purpose thirteen different specimens of milk, which are designated in the following statement of results by the letters A, B, C, etc.

The first column contains the results obtained by the gravimetric method; the second, those obtained by the saponification of the same.

	I.	II.		I.	II.
A.	3.67 per cent.	3.69 per cent.	F.	4.05 per cent.	4.01 per cent.
	3.70	3.67		4.03	4.00
	3.68	3.64	G.	3.59	3.59
B.	3.63	3.62		3.57	3.59
	3.68	3.64	H.	3.35	3.38
	3.65	3.65	I.	3.17	3.18
C.	2.98	2.98	J.	3.37	3.34
	2.99	2.99	K.	3.43	3.40
D.	3.46	3.43	L.	3.65	3.61
	3.44	3.45	M.	3.60	3.59
E.	3.53	3.51			
	3.49	3.50			

The mean of all of the gravimetric determinations is 3.532 per cent.; while the maximum difference in results in any one of the seven cases in which more than one estimation was made is 0.05 per cent. The mean of all of the determinations by saponification is 3.520 per cent. The difference between the mean results by the two methods is only 0.012 per cent. The maximum difference between the weights of any one specimen of butter determined by actual weighing and then by saponification is 0.04 per cent.

It appears, therefore, that the weight of potassium hydroxide required to saponify a given quantity of butter is very constant. The considerable variations in the amounts required to decompose one gram of butter (from 221.5 to 232.4 milligrams), which were found by Koettstorfer,[1] may have been due, we think, to a fact which was afterwards pointed out by Medicus and Scherer,[2] namely, that when butter is fused and allowed to cool without agitation, a partial separation of the constituents takes place, so that the composition of the solidified mass is not homogeneous.

IV.

Five series of determinations were made for the purpose of comparing the new with the gravimetric method. Each series consisted of four estimations by the new, two by the gravimetric method, and a determination by saponification of each of the gravimetric results.

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[1] Zeitschrift für analytische Chemie **18**, 199 and 431.

[2] *Ibid.* **19**, 161.

Each of the series is complete, with the exception of the first, in which one of the gravimetric determinations failed in consequence of the breaking of the flask. In this work every extraction and saponification was repeated in order to demonstrate its completeness. Four of the specimens of milk employed were from the same source, but were obtained on different days.

The different series are designated by the letters A, B, C, D, and E.

In column I are placed the results obtained by the gravimetric method; in column II the results of saponifying the same; and in column III the results obtained by the new method.

I.	II.	III.
	A.	
3.35 per cent.	3.38 per cent.	3.40 per cent.
		3.37
		3.41
		3.41
	B.	
2.97 per cent.	2.98 per cent.	2.97 per cent.
2.99	2.98	2.95
		2.97
		2.95
	C.	
3.46 per cent.	3.43 per cent.	3.47 per cent.
3.44	3.45	3.46
		3.46
		3.50
	D.	
3.53 per cent.	3.51 per cent.	3.48 per cent.
3.49	3.50	3.52
		3.49
		3.48

E.

4.05 per cent.	4.01 per cent.	3.98 per cent.
4.03	4.00	3.97
		3.98
		3.99

V.

To determine whether it is practicable to employ more dilute standard solutions than those we have described, portions of the acid and alkali were diluted to one-half their strength, so that the alkali was approximately quarter normal, while 1 cubic centimeter of the acid was equivalent to the alkali required to saponify 50 milligrams of butter. Three determinations with the original, stronger solutions, and three with the more dilute, were made.

The results were:

I.	II.
3.32 per cent.	3.34 per cent.
3.36	3.32
3.32	3.32

VI.

It was stated in the preliminary article that the amount of potassium hydroxide required to saponify one gram of butter extracted from milk appeared to be more nearly 230 than 227 milligrams. It seemed desirable, therefore, to determine with great care the strength of the specimen of hydrochloric acid which we had standardised by means of butter, and employed with such satisfactory results throughout our work. This was done by means of two specimens of oxalic acid, the one made from pure sugar, the other extracted from so-called chemically pure acid by cold water and recrystallised; also by means of pure calcite. Neither specimen of the oxalic acid left any residue on ignition.

A cubic centimeter of our hydrochloric acid, which had been so standardised that one cubic centimeter of it would neutralise the potassium hydroxide required to saponify 100 milligrams of butter, was found to be equivalent to

22.952 milligrams of KOH (according to acid No. 1).
22.949 milligrams of KOH (according to acid No. 2).
22.958 milligrams of KOH (according to the calcite).

The mean of the three results is 22.953 milligrams, which would indicate that the quantity of potassium hydroxide required to saponify one gram of butter extracted from milk is 229.53 milligrams.

Since we now have, in tropaeolin (oo), an indicator which is not affected by carbonic acid, pure calcite is to be recommended as a substance by which to determine the strength of acids and alkalis. The method of using it is simple and the results quite satisfactory.

The pulverised and weighed calcite is treated with an excess of the acid whose strength is to be ascertained, and a few drops of an aqueous or alcoholic solution of tropaeolin. The excess of the acid is then determined by means of an alkali whose relation to the acid is known. If the solutions are colorless, the change in the color of the tropaeolin, from red to light yellow, is sufficiently distinct to enable one to obtain quite exact results.

VII.

Two series of determinations of three each were made, in order to ascertain whether, when it is desired to make a gravimetric estimation of butter in milk by the usual extraction method, it is as well to dry the milk by means of anhydrous copper sulphate as by evaporation.

The results were:

Milk dried by $CuSO_4$.	Milk dried by Evaporation.
3.67 per cent. of butter.	3.70 per cent. of butter.
3.63 " "	3.65 " "
3.65 " "	3.63 " "

Perhaps this method of drying may also be found useful in dehydrating other materials in which estimations of fat are to be made.

The benzine with which the butter is extracted, the alcohol employed to wash down the sides of the flask during titration, or to dilute the solution of potassium hydroxide, and the water used to dilute the acid to the desired standard, must of course be absolutely neutral, and the testing of the three liquids, especially the alcohol and the water, with phenolphthalein should never be omitted.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

NOTES.

Genesis of the Elements.

Two recent papers[1] by William Crookes, F. R. S., afford a pleasant relief to the usual current of thought in chemical literature. Many a reader of the journals passes very lightly over records of research upon rare elements, feeling that the details of such a field can have little present value either for the practical applications of chemistry or for the development of broad scientific generalisation. The work of Prof. Crookes upon yttrium, however, in which he persevered for years with little hope of reaching a full interpretation of his results, has now borne valuable fruit in the extension of our atomic theory.

The two papers already cited cover the same ground in part and embrace the following points:

1. The nature of the "elements" is open for discussion.

2. The "periodic law" shows that the several elements are closely related as members of one family.

3. Prout's hypothesis suggests an evolution of elements from a simple form of matter; perhaps the "half units" may be explained by the hypothetical "helium."

4. The association in nature of certain groups of similar elements is a remarkable fact which cannot be dismissed by saying that "birds of a feather flock together."

5. Certain compound radicals, as cyanogen, follow the analogy of chemical elements in their behavior. May not our "elements" also be compound radicals in their real nature?

6. Carnelley compares the several groups of our elements to the different series of hydrocarbons, and he even suggests their derivation from two constituents, A and B, whose atomic weights are assumed to be $+12$ and -2.

7. Mills suggests that the elements have been formed during a process of gradual cooling, by successive polimerisation — as I yields I_2, S_2 yields S_6, NO_2 is condensed to N_2O_4, aldehyde is converted into paraldehyde, etc., with evolution of heat.

8. Reynolds represents the periodic classification of the elements by the trace of an oscillating pendulum. Crookes modifies this diagram, representing by the ordinates the gradually diminishing temperature of pre-geologic time, and by the abscissas the increasing and diminishing quantivalence of successive elements, which may be associated with varying amounts of electricity. "Protyle" is a name given to the assumed "original primal matter existing before the evolution of the chemical elements."

9. "Each well-defined element" represents conditions of comparative stability. It does not follow that all atoms of the same element are identical in composition and in aggregate weight.

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[1] "Address to the Chemical Section of the British Association, 1886." "Genesis of the Elements," a lecture delivered February 18, 1887.

Atoms of Ca, for instance, may vary from 39 to 41, or even through a wider range, the accepted atomic weight being the most common value, and the mean value for all calcium atoms.[1]

10. The phosphorescent spectra of didymium and yttrium sulphates present a series of autograph inscriptions from the molecular world; but the strange language could not be interpreted until a Rosetta stone was found in Marignac's "gadolinia." The spectrum of this earth is similar to that of yttria, but *the characteristic "citron band" is omitted*, and the double green band of samaria is added.

11. By an elaborate system of fractionation (based upon the partial precipitation of a dilute solution of yttrium by ammonia) a series of products was obtained, giving no less than five distinct phosphorescent spectra, but all giving the same incandescent spectrum. Three explanations are possible:

a. That which we call the yttrium atom may have a varying structure, always changing to the same form (that of maximum stability) in the electric spark. Crookes regards this view as the most reasonable.

b. Yttrium may consist of eight or nine different elements, yielding the several bands of the phosphorescent spectra.

c. According to de Boisbaudran, the phosphorescent spectra are due to impurities in the yttria.

12. Nordenskiöld (Compt. rend., Nov. 2, 1886) gives the name gadolinia to the crude mixture of yttria, erbia, ytterbia, etc., just as it is precipitated from the minerals containing these rare earths; and he announces that *this mixture has a constant atomic weight.* These elements, then, always occur together in nature, and always in the *same proportions.* With this new fact the supposed evidence that yttrium is an element vanishes; and the same principle may apply to other "elements." The very idea of an element as something absolutely primary and ultimate seems to be growing less and less distinct.

13. "The figures representing the scale of atomic weights may be supposed to represent inversely the scale of a gigantic pyrometer plunged into a cauldron where the elements of suns and worlds are undergoing formation. As the heat sinks the elements generated increase in density and atomic weight."

14. On the other side of the line is room for Carnelley's element of negative atomic weight. Or, is electricity one of the negative elements and luminiferous ether another?

The author, with the earnest hope that chemistry, like biology, may find its Darwin, looks forward to the day when we may foresee the results of every conceivable reaction, and theories may legitimate themselves by the power of prediction.

ROBT. B. WARDER.

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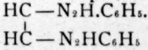
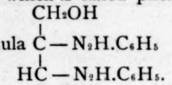
[1] Such fluctuation of the atomic weight of each element, *within very narrow limits*, would exactly account for the small discrepancies observed between the atomic weights as determined by careful experiment, and a precise application of "Prout's law"; for, if we assume that the weight of each *atom* is an exact multiple of that of hydrogen (or of helium), the *average* atomic weight for each element would vary slightly from a normal value.

Probable Synthesis of one of the Sugars.

Although the carbohydrates are among the best known compounds of carbon, and they have been the subject of numerous investigations, no synthesis of any member of the group has been effected up to the present time. In a paper by E. FISCHER and J. TAFEL, recently published, a reaction is described which apparently yields a member of the sugar group — probably glucose. The work was undertaken with the object of studying the changes which poly-acid alcohols undergo when oxidised. By oxidising glycerin a product was obtained which was shown to be either glycerin aldehyde, $CH_2OH.CHOH.COH$, or the isomeric ketone, $CH_2OH.CO.CH_2OH$. To decide between these two possibilities the attempt was made to prepare the aldehyde of glycerin from acroleïn. Bibromacroleïn was made and treated with caustic baryta. Thus there was obtained an easily soluble substance which readily reduces Fehling's solution and has all the properties of an aldehyde-alcohol. It was found impossible to get from the solution a crystallised substance. By treating it with phenylhydrazine, however, an *osazone* of the hexane series of the formula $C_{18}H_{22}N_4O_4$ was obtained. The name *osazone* is given to those hydrazine derivatives which are obtained by treating aldehyde alcohols with phenylhydrazine. All these compounds are derivatives of glyoxal-diphenylhydrazine,  $\begin{array}{l} HC-N_2H.C_6H_5. \\ \;| \\ HC-N_2HC_6H_5 \end{array}$. Thus the glycerin derivative which is called phenylglycerosazone is represented by the formula



$$\begin{array}{l} \;\;CH_2OH \\ \;\;\;| \\ \;\;C-N_2H.C_6H_5 \\ \;\;\;| \\ HC-N_2H.C_6H_5. \end{array}$$

In an earlier paper E. Fischer and A. Steche showed that the action of phenylhydrazine on dextrose and on levulose takes place as represented in the equations:

1. $C_6H_{12}O_6 + C_6H_5.N_2H_3 = C_6H_{12}O_5.N_2H.C_6H_5 + H_2O$;
2. $C_6H_{12}O_5.N_2H.C_6H_5 + 2C_6H_5.N_2H_3 = \underset{\text{Phenyl-glucosazone.}}{C_6H_{10}O_4(N_2H.C_6H_5)_2} + C_6H_5.NH_2 + NH_3 + H_2O$.

The product obtained from bibromacroleïn shows the greatest resemblance to phenylglucosazone. It melts at exactly the same temperature, and cannot be distinguished from it by its appearance. "Nevertheless," say the authors, "in view of the importance of the question we hesitate to assert their identity, and leave the decision to future experiments. This much, however, appears to us to be beyond question, that the described osazone belongs to a member of the sugar group which is formed from bibromacroleïn by treatment with barium hydroxide, as represented in this equation:

$$2C_3H_4Br_2O + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2.$$

We shall, as a matter of course, repeat these experiments on a larger scale and later discuss the process in detail."—(*Berichte der deutschen chemischen Gesellschaft* **20**, 1088.) I. R.